

JC891 U.S. PTO



11/28/00

**IN THE UNITED STATES PATENT AND TRADEMARK  
OFFICE  
REQUEST FOR FILING  
(RULE 53(b)(1))**

### For Design or Utility Applications

Rule 53(b)(1) PATENT APPLICATION:

**(DO NOT USE FOR CIPs)**

☐ Continuation )  
☒ Divisional ) application under 37 CFR 1.53(b)(1)  
 application under 37 CFR 1.53(b)(1)  
 of pending prior application of

Group Art Unit: 1751

Examiner: Hamlin, D.

Inventor(s): OGATA et al.

Parent Appln. No.:

Series Code 

382,589

Serial No. ↑

Atty. Dkt. PM 274506

New M#

**Client Ref**

Parent Filed: August 25, 1999

This Appln. Filed: November 28, 2000

Title: WIDE-RANGE THERMISTOR ELEMENT AND METHOD OF PRODUCING THE SAME

Hon. Commissioner of Patents  
Washington, DC 20231

Date: November 28, 2000

(Parent Matter No. 263319)

Sir:

To effect the above-requested filing today:

1. **Attached** is a copy (**which must be filed**) of the prior application, including:

- ☒ Abstract  
☒ Specification and claims (113 pages; Pages 1a, 1b, 1c, 2-72, 73a, 73b, 73c 74-88, 89a, 89b, 89c, 90-97, 98a, 98b, 98c and 99-105 ) (**must be attached**)  
☒ Drawings (**must be attached if originally filed**): 23 sheet(s)/set): ☐ 1 set informal;  
☒ Formal of size ☒ A4 ☐ 11"

1A. Always X one box, only:

- (1) ☒ Copy of Signed declaration or oath as originally filed in prior application attached
- (2) ☐ NO declaration or fee is enclosed; therefore, this is a filing under Rule 53(f).

2. ☐ This application is hereby filed by less than all of the inventors named in the prior application. Petition is hereby made requesting deletion as inventor(s) of the following who is/are **not** inventor(s) of the invention being claimed in this application (DELETE THE FOLLOWING INVENTOR(S)):

1. \_\_\_\_\_
3. \_\_\_\_\_
5. \_\_\_\_\_
7. \_\_\_\_\_

2. \_\_\_\_\_

4. \_\_\_\_\_

6. \_\_\_\_\_

8. \_\_\_\_\_

2.5 THE INVENTOR(S) FOR THIS NEW APPLICATION IS(ARE):

1. \_\_\_\_\_
3. \_\_\_\_\_
5. \_\_\_\_\_
7. \_\_\_\_\_

2. \_\_\_\_\_  
4. \_\_\_\_\_  
6. \_\_\_\_\_  
8. \_\_\_\_\_

3. The entire disclosure of the prior application is considered as being part of the disclosure of the accompanying application and is hereby incorporated therein by reference thereto.

4. ☒ Priority is claimed under 35 U.S.C. 119/365 based on filing in JAPAN of \_\_\_\_\_ (country)

	<u>Application No.</u>	<u>Filing Date</u>		<u>Application No.</u>	<u>Filing Date</u>
(1)	<u>09-66827</u>	<u>March 19, 1997</u>	(2)	<u>09-156931</u>	<u>June 13, 1997</u>
(3)	<u>09-340313</u>	<u>December 10, 1997</u>	(4)	_____	_____
(5)	_____	_____	(6)	_____	_____

a. ☐ \_\_\_\_\_ (No.) Certified copy/copies attached.

b. ☒ Certified copy/copies previously filed on March 18, 1998 in \_\_\_\_\_  
 U.S. Application No. 09/040,529, filed on March 18, 1998.  
series code ↑ serial no.

c. ☐ Certified copy/copies filed during International stage of PCT/ \_\_\_\_\_ / \_\_\_\_\_

4. (a) ☒ Domestic priority is claimed from 09/040,529, filed March 18, 1998.  
 PCT/  
 (b) ☐ Benefit is claimed of Provisional Application No. 60/\_\_\_\_, filed \_\_\_\_.

5. ☒ Prior application is assigned to DENSO CORPORATION AND NIPPON SOKEN, INC.

by assignment recorded October 22, 1999 Reel 010343 Frame 0871.  
 (Date)

6. ☒ Attached is the following number of Assignments (including original and all later successive ones by different assignors): 1 and respective **new** Cover Sheets. (Do **NOT** file old cover sheets.)

(Assignments in parent **must be refiled** with new Cover Sheets in this continuing application if you want it/them recorded against the continuing application.)

Please return the recorded Assignment to the undersigned.

7. ☒ The power of attorney in the prior application is to Timothy J. Klima, Reg. No. 34,852

(Name and Reg. No.)

whose current address is as in item 8 below.

- a. ☒ Recognize as associate attorney Glenn T. Barrett, Reg. No. 38,705

(Name, Reg. No. and Address)

8. **Address all future communications to Intellectual Property Group of Pillsbury Madison & Sutro LLP, Ninth Floor, East Tower 1100 New York Avenue, N.W., Washington, D.C. 20005-3918**

9. ☒ **Amend the specification** by inserting before the first line the sentence:--This is a  
☐ continuation ☒ division of Application No. 09/382,589, filed August 25, 1999

series code ↑ serial no.

Allowed; which is a continuation-in-part of Appln. Serial No. 09/040,529 Abandoned. --

9. (a) ☐ **Amend the specification** by inserting before the first line: --This application claims the benefit of Provisional Application No. 60/\_\_\_\_, filed \_\_\_\_ --

10. **Small Entity Status** ☒ is **Not** claimed ☐ is claimed (**pre-filing confirmation required**)

(No.) Small Entity Statement(s) (not essential since 9/8/00) were/are:

- ☐ filed in above prior application  
☐ attached.

11. Petition to extend the life of the above prior application to at least the date hereof

(one box) ☐ is being concurrently filed in that prior application (Use Form PAT-111).  
 (must be) ☐ was previously filed in that prior application (Check length of prior extension).  
 (X'd) ☒ is not necessary for copendency (**Double check** before X'ing this box).

12. ☒ **INFORMATION DISCLOSURE STATEMENT:** Attached is Form PTO-1449 listing all of the documents cited by Applicant and the PTO in the parent application(s) relied upon under 35 USC 120 and referenced in item 9 above. Per Rule 98(d) copies of those documents are not required now. Please consider those documents and advise that they have been considered in this new application as by returning a copy of the enclosed Form PTO-1449 with the Examiner's initials in the left column per MPEP 609. .
13. ☐ Attached is a Rule 103(a) Petition to Suspend Action.
14. ☒ **PRELIMINARY AMENDMENT to be entered before fee calculation:** (Do not make amendments here except for correction of improper multiple dependencies or cancellation of whole claims or multiple dependencies for purpose of reducing the filing fee per MPEP §§ 506 and 607; do not cancel all claims).
- Claim 3, line 1, delete 1, delete "1 or";  
 Claim 6, change "claims" to --claim--; and delete "to 5"; and  
 Claim 17, line 2, delete "or 16"

**FILING FEE**

THE FOLLOWING FILING FEE IS BASED ON

->->->->CLAIMS AS FILED AND CHANGED BY PRELIMINARY AMENDMENT IN ITEM 14<-<-<-<-

**NOTE:** If box 1A2 is X'd, do not pay fees,  
 but leave lines 15-22 and 27-32 blank.

**PTO: PLEASE NOTE CLAIM CANCELLATIONS IF BOX 14 ABOVE IS X'D.**

				Large/Small Entity		Fee Code
15. Basic Filing Fee . . . . . Design Application				\$320/\$160		106/26
16. Basic Filing Fee . . . . . Utility Application				\$710/\$355	+710	101/201
17. Total Effective Claims	21	minus 20 =	1	x \$18/\$9	+18	103/203
18. Independent Claims	3	minus 3 =	0	x \$80/\$40	+0	102/202
19. If <u>any proper</u> multiple dependent claim (ignore improper) is present,				\$270/\$135	+0	104/204
20. Subtotal =					<b>\$728</b>	
21. If "petition" box 13 above is X'd, add petition fee. . . . . \$130					+0	122
21A. If box 6 above is X'd, add Assignment recording fee . . . . . \$ 40					+40	581
22. TOTAL FILING FEE ATTACHED =					<b>\$768</b>	

(carry forward to Item 31)

- 22A. ☐ See **NONPUBLICATION REQUEST** under Rule 213(a) attached (PAT-258)
23. ☐ ATTACHED:
24. ☒ Preliminary Amendment attached (to be entered after assigning Appln. No.)
25. ☐ The following PRELIMINARY AMENDMENT is to be entered after assigning Appln. No.:

26.

**ADDITIONAL FEE CALCULATION FOR  
PRELIMINARY AMENDMENT  
PER BOXES 24/25**

	Claims remaining after amendment	Highest number previously paid for	Present Extra	Additional Fee	File Code
			<u>Large/Small Entity</u>		
27.	Total Effective Claims	<u>*15</u>	minus ** <u>21</u> = <u>0</u>	x \$18/\$9 = \$ <u>0</u>	(103/203)
28.	Independent Claims	<u>*9</u>	minus *** <u>3</u> = <u>6</u>	x \$80/\$40 = + <u>480</u>	(102/202)
29.	If amendment enters proper multiple dependent claim(s) into this application for the first time, add (per application) .....			\$270/\$135 + <u>0</u>	(104/204)
30.			ADDITIONAL FEE	\$ <u>0</u>	
31.			plus FEE from item 22 on page 3	+ <u>768</u>	
32.			<b><u>TOTAL FEE ATTACHED</u></b>	\$ <u><u>1248</u></u>	

33. \*If the entry in this space is less than a entry in the next space, the "Present Extra" result is "0"

34. \*\*If the "Highest number previously paid for" (see item 17 above) is less than 20, write "20" in this space

35. If the "Highest number previously paid for" (see item 18 above) is less than 3, write "3" in this space

Our Deposit Account No. 03-3975

Our Order No.	<u>11349</u>	<u>274506</u>
	C#	M#

**CHARGE STATEMENT:** Upon the filing of a Declaration pursuant to Rule 60(b) or 60(d), the Commissioner is hereby authorized to charge any fee specifically authorized hereafter, or any missing or insufficient fee(s) filed, or asserted to be filed, or which should have been filed herewith or concerning any paper filed hereafter, and which may be required under Rules 16-18 (missing or insufficient fee only) now or hereafter relative to this application and the resulting Official document under Rule 20, or credit any overpayment, to our Account/Order Nos. shown above for which purpose a duplicate copy of this sheet is attached.

**This CHARGE STATEMENT does not authorize charge of the issue fee until/unless an issue fee transmittal form is filed.**

**Pillsbury Madison & Sutro LLP  
Intellectual Property Group**

1100 New York Avenue, NW  
Ninth Floor  
Washington, DC 20005-3918  
Tel: (202) 861-3000  
TJK/mjb  
Atty./Sec.

By Atty: Timothy J. Klima/Glenn T. Barrett

Reg. No. 34852/38705

Sig: \_\_\_\_\_

Fax: (202) 822-0944  
Tel: (202) 861-3662

**NOTE No. 1:** File this Request in duplicate with 2 postcard receipts (PAT-103) & attachments

**NOTE No. 2:** Is extension in parent necessary for copendency? **DOUBLE CHECK** Item 11 above.  
If yes, printout Pat-111 and head it in parent.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the patent application of:

**OGATA et al.**

Application No.: Unassigned

Group Art Unit: Unassigned

Divisional Application of Application No. 09/382,589

Filed: Herewith

Examiner: Unassigned

Title: **WIDE-RANGE TYPE THERMISTOR ELEMENT AND METHOD OF PRODUCING THE SAME**

\* \* \* \*

November 28, 2000

**PRELIMINARY AMENDMENT**

Honorable Commissioner of  
Patents  
Washington, D.C. 20231

Sir:

Prior to the initial examination, please amend the above-identified patent application as follows:

**IN THE CLAIMS:**

Please cancel claims 1-7.

Please amend claims 8-14 as follows:

8. (Amended) A method of producing a [the] thermistor element having a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  of a composition  $M^1M^2O_3$  and  $Y_2O_3$ , wherein  $M^1$  is at least one element selected from the elements of the groups IIA and IIIA excluding La in the Periodic Table, and  $M^2$  is at least one element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII [of claim 1], which comprises: performing calcination to obtain  $M^1M^2O_3$  having an average particle diameter larger than that of said  $Y_2O_3$ ;  
mixing said  $M^1M^2O_3$  with said  $Y_2O_3$ ; grinding the mixture to adjust an average particle diameter of the mixture after grinding to an average particle diameter which

is not more than that of said  $Y_2O_3$  before mixing; molding the mixture into an article having a predetermined shape; and sintering the article.

9. (Amended) A method of producing a [the] thermistor element having a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  of a composition  $M^1M^2O_3$  and  $Y_2O_3$ , wherein  $M^1$  is at least one element selected from the elements of the groups IIA and IIIA excluding La in the Periodic Table, and  $M^2$  is at least one element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII, wherein said  $M^1$  is Y, said  $M^2$  are Cr and Mn, and said mixed sintered body is  $Y (CrMn) O_3 \cdot Y_2O_3$  [of claim 4], which comprises:

- mixing an oxide of Cr with an oxide of Mn;
- calcining the mixture at 1000°C or more to obtain  $(Mn_{1.5}Cr_{1.5}) O_4$  having an average particle diameter larger than that of said  $Y_2O_3$ ;
- mixing said  $(Mn_{1.5}Cr_{1.5}) O_4$  with said  $Y_2O_3$ ;
- grinding the mixture to adjust an average particle diameter of the mixture after grinding to an average particle diameter which is not more than that of said  $Y_2O_3$  before mixing;
- molding the mixture into an article having a predetermined shape; and
- sintering the article.

10. (Amended) A method of producing a [the] thermistor element having a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  of a composition  $M^1M^2O_3$  and  $Y_2O_3$ , wherein  $M^1$  is at least one element selected from the elements of the groups IIA and IIIA excluding La in the Periodic Table, and  $M^2$  is at least one element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII, wherein said  $M^1$  is Y, said  $M^2$  are Cr and Mn, and said mixed sintered body is  $Y (CrMn) O_3 \cdot Y_2O_3$  [of claim 5], which comprises:

- mixing an oxide of Cr with an oxide of Mn;
- calcining the mixture at 1000°C or more to obtain  $(Mn_{1.5}Cr_{1.5}) O_4$  having an average particle diameter larger than that of said  $Y_2O_3$ ;
- mixing said  $Mn_{1.5}Cr_{1.5}) O_4$ , said  $Y_2O_3$ , and  $TiO_2$ ;
- grinding the mixture to adjust an average particle diameter of the mixture after grinding to an average particle diameter which is not more than that of said  $Y_2O_3$  before grinding;
- molding the mixture into an article having a predetermined shape; and
- sintering the article.

11. (Amended) A method of producing a thermistor element having a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  of a composition  $M^1M^2O_3$  and  $Y_2O_3$ , wherein  $M^1$  is at least one element selected from the elements of the groups IIA and IIIA excluding La in the Periodic Table, and  $M^2$  is at least one element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII [claim 1], which comprises:

- mixing a raw material of said  $M^2$  with a raw material of said  $M^1$ ;
- grinding the mixture to adjust an average particle diameter of the mixed grind after grinding to an average particle diameter which is not more than that of the raw material of said  $M^1$  before mixing and is not more than 0.5  $\mu m$ ;
- calcining the mixed grind to obtain said  $M^1M^2O_3$ ;
- mixing said  $M^1M^2O_3$  obtained by said calcination with said  $Y_2O_3$ ;
- molding the mixture into an article having a predetermined shape; and
- sintering the article.

12. (Amended) A method of producing a thermistor element having a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  of a composition  $M^1M^2O_3$  and  $Y_2O_3$ , wherein  $M^1$  is at least one element selected from the elements of the groups IIA and IIIA excluding La in the Periodic Table, and  $M^2$  is at least one element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII [of claim 1], which comprises:

- using those containing at least  $Y_2O_3$  as a raw material of said  $M^1$ ;
- mixing a raw material of said  $M^2$  with the raw material of said  $M^1$ ;
- grinding the mixture to adjust an average particle diameter of the mixed grind after grinding to an average particle diameter which is not more than that of the raw material of said  $M^1$  before mixing and is not more than 0.5  $\mu m$ ;
- calcining the mixed grind to obtain a precursor having the same composition as that of said mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$ ;
- molding said precursor obtained by said calcination into an article having a predetermined shape; and
- sintering the article.

13. (Amended) A method of producing a thermistor element having a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  of a composition  $M^1M^2O_3$  and  $Y_2O_3$ , wherein  $M^1$  is at least one element selected from the elements of the groups IIA and IIIA excluding La in the Periodic Table, and  $M^2$  is at least one element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII [of claim 1], which comprises:

- mixing a raw material of said  $M^2$  with a raw material of said  $M^1$ ;

grinding the mixture to adjust an average particle diameter of the mixed grind after grinding to an average particle diameter which is not more than that of the raw material of said  $M^1$  before mixing and is not more than  $0.5\ \mu\text{m}$ ;

calcining the ground mixture to obtain said  $M^1M^2O_3$ ;

mixing said  $M^1M^2O_3$  obtained by said calcination with said  $Y_2O_3$ ;

grinding the mixture to adjust an average particle diameter of the mixture after grinding to an average particle diameter which is not more than that of the raw material of said  $Y_2O_3$  before mixing;

molding the ground mixture into an article having a predetermined shape; and

sintering the article.

14. (Amended) A method of producing a thermistor element having a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  of a composition  $M^1M^2O_3$  and  $Y_2O_3$ , wherein  $M^1$  is at least one element selected from the elements of the groups IIA and IIIA excluding La in the Periodic Table, and  $M^2$  is at least one element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII [of claim 1], which comprises:

using those containing at least  $Y_2O_3$  as a raw material of said  $M^1$ ;

mixing a raw material of said  $M^2$  with the raw material of said  $M^1$ ;

grinding the mixture to adjust an average particle diameter of the mixed grind after grinding to an average particle diameter which is not more than that of the raw material of said  $M^1$  before mixing and is not more than  $0.5\ \mu\text{m}$ ;

calcining the ground mixture to obtain a precursor having the same composition as that of said mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$ ;

grinding said precursor obtained by said calcination to adjust an average particle diameter of said precursor after grinding to an average particle diameter which is not more than that of the raw material  $Y_2O_3$  as the raw material of said  $M^1$  before mixing;

molding the ground precursor into an article having a predetermined shape; and

sintering the article.

Please add new claim 22 as follows:

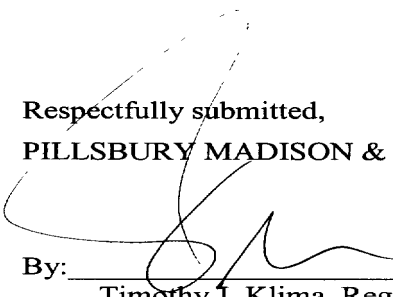
--22. A wide-range type thermistor element according to claim 16, wherein said  $M^1$  is Y, said  $M^2$  and Cr and Mn, said  $M^3$  is Ti, and said  $M^1(M^2M^3)O_3$  is Y (Cr Mn Ti)  $O_3$ .--



**REMARKS**

Claims 8-22 are pending in this application. By this Preliminary Amendment, claims 1-7 are cancelled, claims 8-14 are amended and claim 22 is added. Prompt and favorable consideration on the merits is respectfully requested.

Respectfully submitted,  
PILLSBURY MADISON & SUTRO LLP

By:   
Timothy J. Klima, Reg. No. 34,852  
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(202) 861-3000

SCANNED, # 11

# APPLICATION UNDER UNITED STATES PATENT LAWS

Atty. Dkt. No. PM 274506  
(M#)

Invention: WIDE-RANGE THERMISTOR ELEMENT AND METHOD OF PRODUCING THE SAME

Inventor (s): Itsuhei OGATA  
Takumi KATAOKA  
Eturo YASUDA  
Kaoru KUZUOKA  
Masanori YAMADA

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Ninth Floor  
Washington, DC 20005-3918  
Attorneys  
Telephone: (202) 861-3000

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This is a:

- ☐ Provisional Application
- ☐ Regular Utility Application
- ☒ Continuing Application
  - ☒ The contents of the parent are incorporated by reference
- ☐ PCT National Phase Application
- ☐ Design Application
- ☐ Reissue Application
- ☐ Plant Application
- ☐ Substitute Specification
  - Sub. Spec Filed \_\_\_\_\_
  - in App. No. \_\_\_\_\_ / \_\_\_\_\_
- ☐ Marked up Specification re
  - Sub. Spec. filed \_\_\_\_\_
  - In App. No \_\_\_\_\_ / \_\_\_\_\_

## SPECIFICATION

WIDE-RANGE TYPE THERMISTOR ELEMENT AND  
METHOD OF PRODUCING THE SAME

[illegible]

- 1b -

- CROSS REFERENCE TO RELATED APPLICATIONS

This application is a Continuation-in-Part of National Application No. 09/040,529 filed March 18, 1998 which is incorporated herein by reference and claims priority to Japanese application nos. 09-66827, filed March 19, 1997; 09-156931 filed June 13, 1997; and 09-340313 filed December 10, 1997, all of which are incorporated herein by reference.

09/040,529

5 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a thermistor element which can detect a temperature ranging from room temperature to high temperature of about 1000°C, i.e. so-called wide-range type thermistor element, and the thermistor element is particularly suitable for use in a temperature sensor for an automobile exhaust gas.

2. Description of the Related Art

A thermistor element for a temperature sensor is used in the measurement of a temperature ranging from moderate to high temperature (e.g. 400 to 1300°C, etc.) such as temperature of an automobile exhaust gas, gas flame temperature of gas hot-water supply device, temperature of a heating oven, etc.

Characteristics of this kind of a thermistor element are indicated by the resistivity and resistivity temperature coefficient (temperature dependence of the resistivity). In order to cope with a practical resistivity range of a temperature detecting circuit constituting the temperature sensor, it is desired that the resistivity of the thermistor element is within a predetermined range. Therefore, perovskite materials are exclusively used as those having resistivity characteristics suitable for a wide-range type thermistor element.

As the thermistor element using perovskite material, for example, those described in Japanese Patent Kokai Publication Nos. Hei 6-325907 and Hei 7-201528 are suggested. These thermistor elements are produced by mixing oxides of Y, Sr, Cr, Fe, Ti, etc. in a predetermined composition proportion and calcining the mixture to form a perfect solid solution in order to

realize a thermistor which can used in a wide temperature range.

The resistivity characteristics of the wide-range type thermistor element are indicated by the resistivity and resistivity temperature coefficient. In a normal temperature sensor, it is necessary that the resistivity of the thermistor element is from 50 to 300 k $\Omega$  within a working temperature range in view of the resistivity range of the temperature detecting circuit. In case of affording a heat history from room temperature to 1000°C to the thermistor element, the smaller a change between the resistivity after heat history and the initial resistivity, the better.

In the above Japanese Patent Publications, various thermistor elements of a perfect solid solution are suggested, but only data of the thermistor element resistivity at 300°C or more are disclosed. Therefore, the present inventors have examined the resistivity characteristics at about room temperature of various thermistor elements in the above Japanese Patent Publications.

As a result, regarding those having a resistivity stability in the heat history from room temperature to 1000°C, the resistivity becomes higher in the temperature range from room temperature to 300°C. Therefore, it is impossible to discriminate it from insulation and the temperature can not be detected. On the other hand, regarding those satisfying low resistivity of 50 to 300 k $\Omega$ , the resistivity changes by 10% or more relative to the initial resistivity in the heat history. It has been found that the stability is poor.

There has never been obtained a thermistor element which can satisfy two resistivity characteristics which are contrary to each other, i.e. low resistivity characteristics within a range from room temperature to high temperature of 1000°C and resistivity stability in the heat history (so-called wide-range type thermistor

element).

In the light of the above problems, an object of the present invention is to provide a thermistor element which has stable characteristics (i.e. small  
5 change in resistivity in the heat history from room temperature to 1000°C) and has a resistivity of 50 to 300 kΩ within the temperature range from room temperature to 1000°C.

#### SUMMARY OF THE INVENTION

10 (First aspect)

(A) In the first aspect of the present invention for accomplishing the above object, the present inventors have considered that a conventional thermistor element is composed of a perfect solid solution having a perovskite  
15 type structure but it is difficult for a perfect solid solution as a single compound to satisfy the above resistivity characteristics which are liable to be contrary to each other.

Thus, the above object has been accomplished  
20 by using a novel thermistor material composed of a mixed sintered body prepared by mixing two compounds, i.e. a perovskite material (oxide) having a comparatively low resistivity and a material having a comparatively high resistivity in place of the perfect solid solution.

25 The present inventors have tested and studied various perovskite materials. As a result, it has been found that a composition  $M^1M^2O_3$  ( $M^1$  is at least one element selected from the elements of the groups II and IIIA excluding La in the Periodic Table, and  $M^2$  is at least one  
30 element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII) is preferable as a material having resistivity characteristics which are suitable for accomplishing the above object.

Since La has high moisture absorption  
35 property, there is a problem that La reacts with water in the air to form an unstable hydroxide, which results in breakage of the thermistor element. Therefore, La is not

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used as  $M^2$ .

On the other hand, it has been decided that  $Y_2O_3$  (yttrium oxide), which has a comparatively high resistivity and stabilizes resistivity of the thermistor material, is used as another material to be mixed, as a result of the study.

By preparing a mixed sintered body from  $M^1M^2O_3$  and  $Y_2O_3$ , a thermistor element of a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$ . The term "mixed sintered body" used herein means a sintered body wherein grains constituting the sintered body comprise a mixture of grains of a first component  $M^1M^2O_3$  and grains of a second component  $Y_2O_3$ .

1) That is, this mixed sintered body is a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  of the above  $M^1M^2O_3$  and  $Y_2O_3$ , wherein  $M^1$  is at least one element selected from the elements of the groups IIA and IIIA excluding La in the Periodic Table, and  $M^2$  is at least one element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII in the composition  $M^1M^2O_3$ . More specifically, it can also be represented as  $aM^1M^2O_3 \cdot bY_2O_3$ .

This thermistor element was incorporated into a temperature sensor and the resistivity characteristics of the element were examined. As a result, it could be confirmed that it is stable, that is, a change in resistivity is small (e.g. few %, etc.) even in the heat history from room temperature to  $1000^\circ C$  and the resistivity is from 50 to 300  $k\Omega$  within the temperature range from room temperature to  $1000^\circ C$ .

Therefore, according to this invention, it is possible to provide a thermistor element which can detect a temperature ranging from room temperature to high temperature of  $1000^\circ C$  and has stable characteristics, that is, a change in resistivity is small even in the heat history from room temperature to  $1000^\circ C$ , so-called wide-range type thermistor element.

2) As a result of the study of the present inventors, regarding each element in the above perovskite

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compound  $M^1M^2O_3$ ,  $M^1$  is preferably at least one element selected from Y, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Mg, Ca, Sr, Ba and Sc, and  $M^2$  is preferably at least one element selected from Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Al, Ga, Zr, Nb, Mo, Hf, Ta and W, in view of the practical use.

3) As a result of a further study about a mixing ratio of  $M^1M^2O_3$  and  $Y_2O_3$ , it has been found that the effect of the present invention can be accomplished more certainly if the mixing ratio is within a predetermined range, that is, when a molar fraction of the above  $M^1M^2O_3$  is a and b is a molar fraction of the above  $Y_2O_3$ , these molar fraction a and b satisfy the relations  $0.05 \leq a < 1.0$ ,  $0 < b \leq 0.95$  and  $a + b = 1$  in the composition formula  $aM^1M^2O_3 \cdot bY_2O_3$ .

Since the molar fractions can be changed within a wide range in such way, the resistivity and resistivity temperature coefficient can be widely controlled by appropriately mixing both  $M^1M^2O_3$  and  $Y_2O_3$  and firing the mixture.

4) In the sintered body, a sintering auxiliary is added to improve the sintering property of the respective particles. As a result of the test and study about various sintering auxiliaries, it has been found that it is preferable to use a sintering auxiliary comprising at least one of  $CaO$ ,  $CaCO_3$  and  $CaSiO_3$ , and  $SiO_2$  in case of the mixed sintered body of the present invention. Consequently, a wide-range type thermistor element having excellent sintering density can be obtained.

(B) As a result of the advancement of the test, it has been found that a detected temperature accuracy varies with the sensor in the level within the range from  $\pm 20$  to  $30^\circ C$  in the temperature sensor using the above thermistor element.

Hence, an examination of various conditions in the production step of the thermistor element, such as

compounding, molding and firing or sintering conditions have been advanced for the purpose of improving this temperature accuracy (reduction of scatter in detected temperature accuracy between sensors).

5                   As a result, it has been found that scatter in temperature accuracy arises as follows. That is, since the average particle diameter of  $M^1M^2O_3$  as the perovskite material obtained by the calcination is larger than that of  $Y_2O_3$ , both components are not uniformly mixed to cause  
10 scatter in composition of the mixed sintered body, which results in scatter in resistivity of the thermistor element.

1)           Therefore, the present inventors have considered that uniform mixing of the composition can be  
15 realized if the average particle diameter of  $M^1M^2O_3$  is adjusted to an average particle diameter which is the same as that of  $Y_2O_3$  in the mixed state before calcination, and a test and study have been made. As a result, it has been found that  $M^1M^2O_3$  obtained by the calcination and  $Y_2O_3$  may  
20 be mixed and ground to adjust the average particle diameter of this mixture ( $M^1M^2O_3$  and  $Y_2O_3$ ) to an average particle diameter which is not more than that of  $Y_2O_3$  before mixing.

That is, when using this production  
25 method, uniform mixing is realized by atomization of  $M^1M^2O_3$  and  $Y_2O_3$  and a variation in composition of the mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  is reduced and, therefore, scatter in resistivity of the thermistor element can be reduced. Accordingly, it is possible to provide a wide-  
30 range type thermistor element which can realize a sensor temperature accuracy better than a conventional level within the temperature range from room temperature to  $1000^\circ C$  (small scatter in temperature accuracy between sensors).

35           2)           The mixed sintered body  $Y(CrMn)O_3 \cdot Y_2O_3$  can also be obtained by a method of mixing an oxide of Cr with an oxide of Mn, calcining the mixture at  $1000^\circ C$  or

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more to obtain  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$ , and performing direct mixing/sintering of  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  and  $\text{Y}_2\text{O}_3$  in place of a method of mixing  $\text{Y}(\text{CrMn})\text{O}_3$  with  $\text{Y}_2\text{O}_3$  and sintering the mixture. In this case, the same effect can be exerted by  
5 mixing an oxide of Cr with an oxide of Mn, calcining the mixture at  $1000^\circ\text{C}$  or more to obtain  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  having an average particle diameter larger than that of the above  $\text{Y}_2\text{O}_3$ , mixing this  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  with the above  $\text{Y}_2\text{O}_3$ , grinding the mixture to adjust the average particle  
10 diameter of this mixture to an average particle diameter which is not more than that of the above  $\text{Y}_2\text{O}_3$  before mixing, molding the mixture into an article having a predetermined shape and sintering the article.

3) The mixed sintered body  $\text{Y}(\text{CrMnTi})\text{O}_3 \cdot \text{Y}_2\text{O}_3$   
15 can also be obtained by mixing an oxide of Cr with an oxide of Mn, calcining the mixture at  $1000^\circ\text{C}$  or more to obtain  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$ , and performing mixing and sintering of  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$ ,  $\text{Y}_2\text{O}_3$  and  $\text{TiO}_2$ . In this case, the same effect can be obtained by mixing an oxide of Cr with an  
20 oxide of Mn, calcining the mixture at  $1000^\circ\text{C}$  or more to obtain  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  having an average particle diameter larger than that of the above  $\text{Y}_2\text{O}_3$ , mixing this  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  with the above  $\text{Y}_2\text{O}_3$  and  $\text{TiO}_2$ , grinding the mixture to adjust the average particle diameter of this  
25 ground mixture to an average particle diameter which is not more than that of the above  $\text{Y}_2\text{O}_3$  before mixing, molding the mixture into an article having a predetermined shape and sintering the article.

(C) Furthermore, an examination of the production  
30 method of the thermistor element has been advanced for the purpose of improving the detected temperature accuracy of the temperature sensor using the thermistor element of the present invention. As a result, it has been found that scatter in composition of  $\text{M}^1\text{M}^2\text{O}_3$  itself obtained by the  
35 calcination exerts an influence on scatter in composition of the mixed sintered body  $\text{M}^1\text{M}^2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  (i.e. scatter in resistivity of the thermistor element).

Now, the cause of scatter in the composition of  $M^1M^2O_3$  obtained by the calcination in the method of producing the mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  will be described by way of the example wherein  $M^1 = Y$  and  $M^2 = Cr$  and Mn, i.e. example using  $Y(Cr_{0.5}Mn_{0.5})O_3$ .

For example,  $Y(Cr_{0.5}Mn_{0.5})O_3$  is prepared as follows (see Fig. 20).  $Y_2O_3$  (average particle diameter: about  $1 \mu m$ ) as a source material of  $M^1$ , and  $Cr_2O_3$  (average particle diameter: about  $4 \mu m$ ) and  $Mn_2O_3$  (average particle diameter: about  $7 \mu m$ ) as source materials of  $M^2$  are compounded in a molar ratio  $Y:Cr:Mn = 1:0.5:0.5$  (compounding 1), mixed and ground by using a ball mill, and then this mixture is calcined at  $1000^\circ C$  or more to obtain  $Y(Cr_{0.5}Mn_{0.5})O_3$ .

The present inventors have found that a problem lies in the mixing and grinding using a ball mill in the above step. That is, according to the mixing and grinding using a ball mill, the average particle diameter after the mixing and grinding is limited to about  $2 \mu m$  and the average particle diameter of  $Cr_2O_3$  and that of  $Mn_2O_3$  are larger than that of  $Y_2O_3$ .

Accordingly,  $Y(Cr_{0.5}Mn_{0.5})O_3$  obtained by the calcination reaction of the mixture of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  becomes a mixture containing a composition shifted from  $Y:Cr:Mn = 1:0.5:0.5$  due to a difference in particle diameter of each raw material, e.g. various compositions from composition of  $Y:Cr:Mn = 1:0.6:0.4$  to composition of  $Y:Cr:Mn = 1:0.4:0.6$ .

Since these compositions, from a composition of  $Y:Cr:Mn = 1:0.6:0.4$  to a composition of  $Y:Cr:Mn = 1:0.4:0.6$ , have different resistivity and resistivity temperature coefficient ( $\beta$  value), the resistivity varies with the element to cause scatter in element resistivity.

In case that a part of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  as the raw material (shifted from the composition ratio) is remained as an unreacted matter, scatter in element resistivity arises.

The present inventors have intensively studied problems such as scatter in composition of  $M^1M^2O_3$ , obtained in the step before obtaining  $M^1M^2O_3$ , by the calcination, presence of the unreacted matter, etc.

5 As a result, it has been found that the above drawbacks can be inhibited and the temperature accuracy becomes  $\pm 10^\circ\text{C}$  or less if the raw material of  $M^2$  and that of  $M^1$  are mixed and ground by using a medium stirring mill having a grinding capability higher than that of a ball  
10 mill and atomization is performed so that the average particle diameter of the raw material mixture (mixed grind) after mixing and grinding is adjusted to an average particle diameter which is not more than that of the raw material of  $M^1$  and is not more than  $0.5 \mu\text{m}$ .

15 The method of producing the thermistor element of the present invention has been accomplished based on the above finding.

1) That is, in this invention, the raw material of  $M^2$  and the raw material of  $M^1$  are mixed and  
20 ground to adjust the average particle diameter of this mixed grind to an average particle diameter which is not more than that of the raw material of  $M^1$  before mixing and is not more than  $0.5 \mu\text{m}$  in the mixing step of mixing and grinding the raw material of  $M^2$  and the raw material of  $M^1$ .  
25 Thereafter,  $M^1M^2O_3$  is obtained by calcination, and the  $M^1M^2O_3$  and  $Y_2O_3$  are then mixed. The mixture is molded into an article having a predetermined shape and then sintered.

According to the present invention, since uniform mixing of the composition can be realized by  
30 uniform atomization of the raw materials of  $M^1$  and  $M^2$ , reduction of scatter in composition of  $M^1M^2O_3$  formed after calcination and inhibition of the existence of the raw material unreacted reaction matter can be realized. Therefore, scatter in resistivity of the thermistor  
35 element can be reduced.

Accordingly, it is possible to provide a wide-range type thermistor element which realizes a sensor

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5 When using those containing at least  
Y<sub>2</sub>O<sub>3</sub> as the raw material of M<sup>1</sup>, a thermistor element can  
also be obtained by mixing the raw material of M<sup>1</sup> and the  
raw material of M<sup>2</sup>, grinding the mixture, calcining the  
mixture to form a precursor having the same composition as  
10 that of the desired mixed sintered body M<sup>1</sup>M<sup>2</sup>O<sub>3</sub> · Y<sub>2</sub>O<sub>3</sub>,  
molding this precursor into an article having a  
predetermined shape, and sintering the article.

2) In addition, according to the production method using precursors containing at least  $Y_2O_3$ , the above precursor is obtained by mixing the raw material of  $M^1$  and the raw material of  $M^2$ , grinding the mixture to adjust the average particle diameter of this mixed grind to an average particle diameter which is not more than that of the raw material of  $M^1$  before mixing and which is 0.5  $\mu$  m or less, and calcining the mixed grind.

Consequently, since uniform mixing of the composition can be realized by uniform atomization of the raw materials of  $M^1$  and  $M^2$ , reduction of scatter in composition of the precursor formed after calcination and inhibition of the existence of the raw material unreacted reaction matter can be realized. As a result, scatter in composition of the mixed sintered body having the same

3) A method of mixing a raw material of  $M^2$  with a raw material of  $M^1$ , grinding the mixture to adjust an average particle diameter of the mixed grind to an average particle diameter which is not more than that of the raw material of  $M^1$  before mixing and is also not more than  $0.5 \mu m$ , calcining the ground mixture to obtain  $M^1M^2O_3$ ,

4) Similarly, a method of using precursors containing at least  $Y_2O_3$  as a raw material of  $M^1$ , mixing a raw material of  $M^2$  with the raw material of  $M^1$ , grinding the mixture to adjust an average particle diameter of the mixed grind after grinding to an average particle diameter which is not more than that of the raw material of  $M^1$  before mixing and is also not more than  $0.5 \mu m$ , calcining the ground mixture to obtain a precursor having the same composition as that of the mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$ ,

grinding the precursor obtained by the calcination to adjust an average particle diameter of the precursor after grinding to an average particle diameter which is not more than that of the raw material  $Y_2O_3$  as the raw material of  $M^1$  before mixing, molding the ground precursor into an article having a predetermined

shape, and calcining the article is a combination of the above production method (B) and (C). According to this method, since the uniform mixing of  $M^1M^2O_3$  and  $Y_2O_3$  can be realized and a variation in composition of the mixed  
5 sintered body can be reduced in the molding and sintering as the following step, by atomizing the precursor  $M^1M^2O_3 \cdot Y_2O_3$  having the same composition as that of the mixed sintered body to a level smaller than the average particle diameter of  $Y_2O_3$  as the raw material of  $M^1$ ,  
10 scatter in resistivity of the thermistor element can be reduced.

That is, according to this element, scatter in resistivity of the thermistor element can be reduced to a higher level.

15 (Second aspect)

The material of the above conventional thermistor element is a perfect solid solution having a perovskite type structure. In case of a  $YCrO_3$  perovskite type material, the valence of a Y ion of A site or Cr of a B  
20 site ion is controlled by other element ions so as to optionally control the resistivity and resistivity temperature coefficient. The present inventors have considered that the crystal structure becomes unstable by increasing the substitution element ions according to this  
25 method and it is difficult to satisfy the resistance characteristics which are liable to be contrary to each other.

Hence, the present inventors have decided to accomplish the above object by selecting the element  
30 capable of controlling the resistivity and resistivity temperature coefficient of a wide-range type thermistor element which can maintain the stability of the crystal structure and realize the stability of the resistivity even in the heat history, in a small amount to be  
35 substituted.

1) The present inventors have tested and studied various perovskite materials. As a result, it has been

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found that a novel composition  $M^1(M^2M^3)O_3$  ( $M^1$  is at least one element selected from the elements of the groups II and IIIA excluding La in the Periodic Table, and  $M^2$  and  $M^3$  respectively represent at least one element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII, wherein the relation of  $1 < b < 0.1$  is satisfied when a molar fraction of  $M^2$  is a, a molar fraction of  $M^3$  is b and  $a + b = 1$  in  $M^1(M^2M^3)O_3$ ) is preferable as a material having resistivity characteristics which are suitable for accomplishing the above object.

Since La has high moisture absorption property, there is a problem that La reacts with water in the air to form an unstable hydroxide, which results in breakage of the thermistor element. Therefore, La is not used as  $M^1$ .

This wide-range type thermistor element was incorporated into a temperature sensor and the resistivity characteristics of the element were examined. As a result, it could be confirmed that it is stable, that is, a change in resistivity is small even in the heat history from room temperature to  $1000^\circ\text{C}$  and the resistivity is from 60 to  $300\text{ k}\Omega$  within the temperature range from room temperature to  $1000^\circ\text{C}$ .

Therefore, according to the above invention, it is possible to provide a wide-range type thermistor element which can detect a temperature ranging from room temperature to high temperature of  $1000^\circ\text{C}$  and has stable characteristics, that is, a change in resistivity is small even in the heat history from room temperature to  $1000^\circ\text{C}$ .

2) As a result of the study of the present inventors, regarding each element in the above perovskite compound  $M^1(M^2M^3)O_3$ ,  $M^1$  is preferably at least one element selected from Y, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Mg, Ca, Sr, Ba and Sc, and  $M^2$  and  $M^3$  preferably represent at least one element selected from Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga, Zr, Nb, Mo, Zr, Hf, Ta and W, in view of practical use.

3) Furthermore, it has been found that the above effect can be accomplished, more certainly, if the relation of  $1 < b < 0.1$  is satisfied when a molar fraction of  $M^2$  is  $a$ , a molar fraction of  $M^3$  is  $b$  and  $a + b = 1$  in perovskite compound  $M^1(M^2M^3)O_3$  where  $M^1$  is Y,  $M^2$  comprises Cr and  $M^3$  and  $M^3$  is Ti, i.e.,  $Cr(MnTi)O_3$ .

4) In the sintering of the above compound  $M^1(M^2M^3)O_3$ , a sintering auxiliary is added to improve the sintering property of the respective particles. As a result of the test and study of various sintering auxiliaries, it has been found that it is preferable to use a sintering auxiliary comprising at least one of  $CaO$ ,  $CaCO_3$  and  $CaSiO_3$ , and  $SiO_2$  in case of the sintered body of the invention of this aspect. Consequently, according to this aspect, a thermistor element having excellent sintering density in the above compound  $M^1(M^2M^3)O_3$  can be obtained.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a flow chart illustrating a production step of a thermistor element of Example 1 of the present invention.

Fig. 2 is a schematic diagram illustrating the thermistor element in Example 1.

Fig. 3 is a schematic sectional view illustrating a temperature sensor using the thermistor element of Fig. 2.

Fig. 4 is a schematic sectional view illustrating a metal pipe of the temperature sensor of Fig. 3.

Figs. 5 to 25 are flow charts illustrating respectively a production step of thermistor elements of Examples 2 to 11 and 15 to 25 of the present invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

(First aspect)

(First embodiment)

In the perovskite material  $M^1M^2O_3$  of the present invention, the element  $M^1$  can be selected, for example, from Mg, Ca, Sr and Ba of the group IIA and Y, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb and Sc of the group IIIA

excluding La.

The element  $M^2$  can be selected, for example, from Zn of the group IIB, Al and Ga of the group IIIB, Ti, Zr and Hf of the group IVA, V, Nb and Ta of the group VA, Cr, Mo and W of the group VIA, Mn, Tc and Re of the group VIIA, and Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt of the group VIII.

The production step of the mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  is roughly divided into a first preparation step of obtaining  $M^1M^2O_3$  by calcination and a second preparation step of compounding the resulting  $M^1M^2O_3$  and  $Y_2O_3$  to form a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$ , to thereby obtain a thermistor element.

In the first preparation step,  $M^1M^2O_3$  can be obtained by compounding an oxide of  $M^1$ , ( $M^1O_x$ ), and an oxide of  $M^2$ , ( $M^2O_x$ ), as the raw materials of  $M^1$  and  $M^2$  (compounding 1), mixing and grinding the mixture (mixing step) and calcining the ground mixture (e.g. at about 1000 to 1500°C, etc.) (calcination step).

When  $M^1$  is Y, an oxide ( $M^2O_x$ ) which does not contain Y but contains only  $M^2$ , e.g. spinel compound  $(Mn_{1.5}Cr_{1.5})O_4$  wherein  $M^2$  are Mn and Cr, may be obtained even if  $YM^2O_3$  is not previously obtained in the first preparation step.

In the second preparation step, the resulting  $M^1M^2O_3$  or  $M^2O_x$  is compounded with  $Y_2O_3$  so that the desired resistivity and resistivity temperature coefficient are obtained (compounding 2). In the compounding of  $M^2O_x$  and  $Y_2O_3$ , the compounding is performed so that Y of  $Y_2O_3$  is incorporated into the  $M^2O_x$  site in the solid state to form a perovskite compound  $YM^2O_3$  in case of the sintering described hereinafter.

In the compounding of  $M^1M^2O_3 + Y_2O_3$ , or  $M^2O_x + Y_2O_3$ , an oxide of  $M^1$  or  $M^2$  or a double oxide of  $M^1$  and  $M^2$  (e.g.  $TiO_2$ ,  $YTiO_3$ , etc.) may be further compounded so that the desired resistivity and resistivity temperature coefficient can be obtained. Also, in this case, the compounding is performed so that  $M^1$  or  $M^2$  from these additives is

Then, a thermistor element of  $M^1M^2O_3 \cdot Y_2O_3$  is obtained  
5 by grinding the compounded mixture  $M^1M^2O_3 + Y_2O_3$  (or  $M^2O_x + Y_2O_3$ ) (grinding step) to form a powder, incorporating a lead wire of Pt, etc., molding the powder into an article having a predetermined shape in a mold (molding step), and performing the above sintering (e.g. 1500°C or more, etc.)  
10 (sintering step).

The thermistor element thus obtained is a mixed sintered body prepared by uniformly mixing  $M^1M^2O_3$  as the perovskite compound and  $Y_2O_3$  via grain boundaries.

$\beta$  is represented by the equation:  $\beta (K) = \ln (R/R_0)/(1/K - 1/K_0)$ . In the equation,  $\ln$  represents a common logarithm, and  $R$  and  $R_0$  respectively represent a resistivity of the thermistor element at room temperature (300K) and that at 1000°C (1273K) in air. In addition, the change in resistivity  $\Delta R$  represents a change in resistivity of the temperature sensor in a high-temperature durability test wherein each temperature sensor is allowed to stand in the air at 1100°C for 100

hours, and is represented by the equation  $\Delta R (\%) = (R'_t/R_t) \times 100 - 100$ . Incidentally,  $R_t$  represents an initial resistivity at a predetermined temperature  $t$  (e.g. 400°C, etc., and  $R'_t$  represents a resistivity at a predetermined temperature  $t$  after standing for a predetermined time.

As a result, it could be confirmed that  $R_t$  is from 50 to 100 k $\Omega$  and  $\beta$  can be adjusted within the range from 2000 to 4000K and, furthermore,  $\Delta R$  can realize a level of about few %.

In order to realize the above  $R_t$  range and respective values of  $\beta$  and  $\Delta R$ , more certainly, the molar fractions  $a$  and  $b$  in  $aM^1M^2O_3 \cdot bY_2O_3$  preferably satisfy the relations  $0.05 \leq a < 1.0$ ,  $0 < b \leq 0.95$  and  $a + b = 1$ .

Therefore, according to this embodiment, it is possible to provide a wide-range type thermistor element which can detect a temperature ranging from room temperature to high temperature of 1000°C and has stable characteristics, that is, a change in resistivity is small even in the heat history from room temperature to 1000°C.

Since the resistivity temperature coefficient  $\beta$  can be controlled to 2000-4000K smaller than that of a conventional thermistor element, scatter in resistivity with a variation in temperature can be reduced.

This embodiment will be described in more detail by way of Examples 1 to 6 and Comparative Examples 1 to 2 described hereinafter.

(Second embodiment)

This second embodiment provides a method of producing a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$ , and has first and second preparation steps, like the above first embodiment. Furthermore, the second embodiment has the following feature, in addition to the above first embodiment.

That is, in the above second preparation step, the average particle diameter of the resulting mixture is adjusted to an average particle diameter which is not more



particle diameter of the above mixture is adjusted to the average particle diameter (about  $1.0\mu\text{ m}$ ) of  $\text{Y}_2\text{O}_3$  before mixing.

As a grinding means for reducing the average particle diameter, a medium stirring mill can be used. As a grinding means of the medium stirring mill, a ball (e.g.  $1\text{mm}\phi$  or less, etc.) made of  $\text{ZrO}_2$  can be used.

Therefore, according to this second embodiment, since uniform mixing can be realized by atomization of  $\text{M}^1\text{M}^2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ , or  $\text{M}^2\text{O}_x$  and  $\text{Y}_2\text{O}_3$  and a variation in composition of the mixed sintered body  $\text{M}^1\text{M}^2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  can be reduced, scatter in the resistivity of the thermistor element can be reduced.

Accordingly, it is possible to provide a wide-range type thermistor element which can realize a sensor temperature accuracy better than a conventional level within the temperature range from room temperature to  $1000^\circ\text{C}$  (a small scatter in temperature accuracy between sensors).

The second embodiment will be described in more detail by way of Examples 7 to 14 described hereinafter.

(Third embodiment)

This third embodiment provides a method of producing a mixed sintered body  $\text{M}^1\text{M}^2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , and has first and second preparation steps, like the above first embodiment, but differs from the above first embodiment in the following respect.

That is, the third embodiment is characterized by mixing and grinding the raw material of  $\text{M}^2$  and raw material of  $\text{M}^2$  to adjust the average particle diameter of this mixed grind to an average particle diameter which is not more than that of the raw material of  $\text{M}^1$  before mixing and is not more than  $0.5\mu\text{ m}$  in the step of mixing and grinding the oxide of  $\text{M}^1$  ( $\text{M}^1\text{O}_x$ ) and the oxide of  $\text{M}^2$  ( $\text{M}^2\text{O}_x$ ) as the raw materials of  $\text{M}^1$  and  $\text{M}^2$  (mixing step) and calcining the mixed grind to obtain  $\text{M}^1\text{M}^2\text{O}_3$  alone or a precursor  $\text{M}^1\text{M}^2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  of the mixed sintered body.

Accordingly, the method of producing the mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  in this embodiment includes two production methods wherein the calcined matter obtained in the first preparation is a precursor  $M^1M^2O_3 \cdot Y_2O_3$  having the same composition as that of the mixed sintered body, or  
5  $M^1M^2O_3$  alone. The former is a first production method whereas the latter is a second production method.

As described above, the precursor  $M^1M^2O_3 \cdot Y_2O_3$  is that wherein  $Y_2O_3$  containing excess Y in an amount larger than a stoichiometric amount (theoretical amount) is combined  
10 with  $M^1M^2O_3$  in the above  $M^1M^2O_3$  (perovskite structure), and has the same composition as that of the desired mixed sintered body.

There are some overlapped portions between this  
15 third embodiment and the above first embodiment. Therefore, the different portion will be described, exclusively.

According to the first production method, in the first preparation step, those containing at least  $Y_2O_3$  as  
20 the raw material of  $M^1$  and an oxide of  $M^2$  ( $M^2O_x$ ) as the raw material of  $M^2$  are compounded, mixed, ground and then calcined (e.g. 1000 to 1500°C, etc.) to obtain a precursor  $M^1M^2O_3 \cdot Y_2O_3$ .

In case of the above mixing and grinding (mixing  
25 step), the average particle diameter of the mixed grind after grinding is adjusted to an average particle diameter which is not more than that of the raw material of  $M^1$  before mixing and is not more than 0.5  $\mu$  m by using a medium stirring mill described in the above second  
30 embodiment, and then the mixed grind is calcined to obtain a precursor.

Thereafter, in the second preparation step, the above precursor is compounded to the desired amount. After grinding and incorporating a lead wire of Pt, the  
35 precursor is molded into an article having a desired shape and then calcined (e.g., at 1500°C or higher) to obtain a thermistor element of a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$ .

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According to the second production method, in the first preparation step, an oxide of  $M^1$  ( $M^1O_x$ ) and an oxide of  $M^2$  ( $M^2O_x$ ) as the raw materials of  $M^1$  and  $M^2$  are compounded, mixed, ground and then calcined (e.g. at about 1000 to 1500°C, etc.) to obtain  $M^1M^2O_3$ .

In case of the mixing and grinding (mixing step), the average particle diameter of the mixed grind after grinding is adjusted to an average particle diameter which is not more than that of the raw material of  $M^1$  before mixing and is not more than 0.5  $\mu$  m by using a medium stirring mill described in the above second embodiment.

Thereafter, in the second preparation step,  $M^1M^2O_3$  and  $Y_2O_3$  are compounded in a desired amount and then treated in the same manner as in the first production method to obtain a thermistor element of a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$ .

Consequently, since uniform mixing of the composition is realized by uniform atomization of the raw materials of  $M^1$  and  $M^2$ , reduction of a variation in  $M^1M^2O_3$  formed after calcination and a mixed sintered body and inhibition of the existence of the unreacted raw material can be realized and scatter in the resistivity of the thermistor element can be reduced.

Accordingly, it is possible to provide a wide-range type thermistor element which can detect a temperature ranging from room temperature to high temperature of 1000°C and has stable characteristics, that is, a change in resistivity is small in the heat history from room temperature to 1000°C.

In the first and second production methods, the grinding in the grinding step of the second preparation step may be grinding using a ball mill, but may also be performed by using a medium stirring mill, as in the second embodiment.

That is, in the first production method, the precursor obtained by the calcination is mixed and ground to adjust the average particle diameter of the precursor

after grinding to an average particle size which is not more than that of  $Y_2O_3$  before mixing in the first preparation step. On the other hand, in the second production method,  $M^1M^2O_3$  obtained by the calcination and  $Y_2O_3$  are mixed and ground to adjust the average particle diameter of the precursor after grinding to an average particle size which is not more than that of  $Y_2O_3$  before mixing.

Consequently, in the molding and calcining step as the post step of the grinding step, uniform mixing of  $M^1M^2O_3$  and  $Y_2O_3$  is performed, in addition to the above-described effect of the third embodiment of the present invention, and a variation in composition of the mixed sintered body is reduced. Therefore, scatter in the resistivity of the thermistor element can be reduced.

Accordingly, scatter in resistivity of the thermistor element can be reduced to a higher level in comparison with the method of the second embodiment of the present invention, thereby making it possible to provide a wide-range type thermistor element with good sensor temperature accuracy (a small scatter in temperature accuracy between sensors).

The temperature sensors using the wide-range type thermistor elements of the second and third embodiments of the present invention are suitable for use in map control devices to which high temperature accuracy is required, e.g. a temperature monitor for an oxygen sensor for automobile exhaust gas, etc. because the temperature accuracy is controlled within  $\pm 10^\circ C$  or less.

The third embodiment of the present invention will be described in more detail by way of Examples 15 to 20 and Comparative Example 3 described hereinafter.

The above first embodiment, second embodiment and third embodiment of the present invention will be described in more detail by way of the following Examples 1 to 6 and Comparative Examples 1 and 2, Examples 7 to 14, and Examples 15 to 20 and Comparative Example 3,



5           The present inventors have studied the above  
respective characteristics of the thermistor elements  
using various  $M^1(M^2M^3)O_3$  and temperature sensors. As a  
result, it has been found that if b satisfies the  
relation:  $0 < b < 0.1$  when a is a molar fraction of  $M^2$ , b  
10 is a molar fraction of  $M^3$  and a and b satisfies the  
relation:  $a + b = 1$ , it is possible to provide a wide-  
range type thermistor element which can detect a  
temperature ranging from room temperature to a high  
temperature of  $1000^\circ\text{C}$  and has stable characteristics, that  
15 is, a change in resistivity is small in the heat history  
from room temperature to  $1000^\circ\text{C}$ .

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A flow chart illustrating a production step of the thermistor element of Example 1 is shown in Fig. 1. This

production step is roughly divided into a first preparation step from compounding 1 to formation of  $Y(Cr_{0.5}Mn_{0.5})O_3$ , and a second preparation step from compounding of the resulting  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$  to completion of a thermistor element.

In the first preparation step,  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  (purity of all components is not less than 99.9%) are first prepared and then weighed so that a molar ratio Y:Cr:Mn becomes 2:1:1 to make 500 g as the total amount (compounding 1).

Using a resin pot (volume: 5 liter) containing  $Al_2O_3$  or  $ZrO_2$  pebbles having a diameter of 15 mm $\phi$  (2.5 kg) and pebbles having a diameter of 20 mm $\phi$  (2.5 kg) as a ball mill to mix these weighed substances, the total amount of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  is charged in the pot, in order to mix these weighed substances. After adding 1500 cc of purified water, the mixture was mixed at 60 rpm for 6 to 12 hours (mixing step).

A mixed slurry of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  obtained after a mixing treatment is transferred to a porcelain evaporating dish, and then dried by using a hot-air dryer at 150°C for 12 hours or more to obtain a mixed solid of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$ . Subsequently, this mixed solid is roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a mixed powder of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$ .

In the calcination step, this mixed powder is charged in a crucible made of 99.3%  $Al_2O_3$  and then calcined in a high-temperature oven in the air at 1100 to 1300°C for 1 to 2 hours to obtain  $Y(Cr_{0.5}Mn_{0.5})O_3$ .  $Y(Cr_{0.5}Mn_{0.5})O_3$  as a bulk solid obtained in the calcination was roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a powder.

This  $Y(Cr_{0.5}Mn_{0.5})O_3$  shows low resistivity and a low resistivity temperature coefficient at 1000 to 4000K when used alone as a thermistor material. As a wide-range type thermistor material, this  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$ , as



(pure platinum)) having a size of 0.3 mm $\phi$  in outer diameter x 10.5 mm in length, the lead wire is inserted and the thermistor raw material is molded in a mold having an outer diameter of 1.74 mm $\phi$  under a pressure of about 1000 kgf/cm<sup>2</sup> to obtain a molded article of a thermistor element (provided with a lead wire) having an outer diameter of 1.75 mm $\phi$  .

In the sintering step, the molded article of the thermistor element is arranged on a corrugated setter made of Al<sub>2</sub>O<sub>3</sub> and then sintered in the air at 1400 to 1600°C for 1 to 2 hours to obtain a thermistor element having an outer diameter of 1.60 mm $\phi$  of a mixed sintered body aY(Cr<sub>0.5</sub>Mn<sub>0.5</sub>)O<sub>3</sub> · bY<sub>2</sub>O<sub>3</sub> .

The resulting thermistor element 1 is shown in Fig. 2. The respective ends of two parallel lead wires 11, 12 are embedded in a cylindrical element portion 13 having an outer diameter of 1.60 mm $\phi$  . This thermistor element 1 is incorporated into a typical temperature sensor shown in Fig. 3 and Fig. 4 to give a temperature sensor.

The thermistor element 1 is disposed in a cylindrical heat-resistant metal case 2, as shown in Fig. 3. The lead wires 11, 12 are respectively connected to lead wires 31, 32 which pass through a metal pipe 3. As shown in Fig. 4, the metal pipe 3 is filled with a magnesia powder 33 to secure the insulating properties of the lead wires 31, 32 in the metal pipe 3. In such way, the temperature sensor is constructed.

In this Example, Examples 2 to 20 and Comparative Examples 1 to 3, thermistor elements and temperature sensors to be made have the same structure as that of thermistor elements and temperature sensors shown in Fig. 2 to Fig. 4 and the description will be omitted. Incidentally, the material composition of a mixed sintered body constituting the element portion 13 varies with each Example, as a matter of course.

Furthermore, in the above second preparation step, Y(Cr<sub>0.5</sub>Mn<sub>0.5</sub>)O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> are weighed so that a compounding

molar ratio  $Y(Cr_{0.5}Mn_{0.5})O_3:Y_2O_3$  becomes 95:5 and 5:95. Then, a thermistor element is made in the same procedure as described above and is incorporated into a temperature sensor. The respective elements of this Example are referred to as an element No. 1, an element No. 2 and an element No. 3 in the sequence of the compounding molar ratio (corresponding to a:b) of  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$ , e.g. 38:62, 95:5 and 5:95.

The temperature sensors made by incorporating the elements No. 1 to No. 3 were put in a high-temperature oven and temperature characteristics of the resistivity were evaluated within the range from room temperature (27°C) to 1000°C. The evaluation results are shown in Table 1.

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Table &lt;Example 1&gt;

No.	Raw material composition (mol %)		Resistivity (k $\Omega$ )		Resistivity temperature coefficient (K)	Change in resistivity (%)
	Y(Cr <sub>0.5</sub> Mn <sub>0.5</sub> )O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Room temperature (27°C)	1000°C		
1	38	62	50	0.14	2450	-5.0
2	95	5	30	0.10	2240	-4.0
3	5	95	100	0.20	2440	-4.0

As shown in Table 1, the wide-range type thermistor element of Example 1 shows low resistivity of 50 to 100 k $\Omega$  required as a temperature sensor within the range where the molar fraction ( $a + b = 1$ ) of  $aY(CrMn)O_3 \cdot bY_2O_3$  satisfy the relations:  $0.05 \leq a < 1$  and  $0 < b \leq 0.95$ , and also shows a resistivity temperature coefficient  $\beta$  of 2000 to 4000K, and it is possible to widely control the resistivity and resistivity temperature coefficient. Therefore, it is possible to detect a temperature ranging from room temperature to high temperature of 1000°C.

As is apparent from the results of the high-temperature durability test (change in resistivity), a wide-range type thermistor material having stable characteristics (e.g. small change in resistivity), etc.) can be provided.

(Example 2)

In Example 2, a mixed sintered body of  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$  is obtained from  $(Mn_{1.5}Cr_{1.5})O_4$  and  $Y_2O_3$ . In this Example, since Y of  $Y_2O_3$  is incorporated into  $(Mn_{1.5}Cr_{1.5})O_4$  in the solid state, Y is selected as  $M^1$  and Cr and Mn are selected as  $M^2$  in  $M^1M^2O_3$ .

A flow chart illustrating a production step of the thermistor element of Example 2 is shown in Fig. 5. This production step is roughly divided into a first preparation step from compounding 1 to formation of  $(Mn_{1.5}Cr_{1.5})O_4$ , and a second preparation step from compounding (compounding 2) of the resulting  $(Mn_{1.5}Cr_{1.5})O_4$  and  $Y_2O_3$  to completion of a thermistor element.

In the first preparation step,  $Cr_2O_3$  and  $Mn_2O_3$  (purity of all components is not less than 99.9%) are first prepared and then weighed so that a molar ratio Cr:Mn becomes 1:1 to make 500 g as the total amount (compounding 1).

Subsequently,  $Cr_2O_3$  and  $Mn_2O_3$  as compounded are subjected to a treatment such as mixing, drying, grinding, firing, etc. in the same manner as in Example 1 to obtain

(Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub>. Then, (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> is roughly ground and passed through a sieve (# 30 mesh) to obtain a powder. As a wide-range type thermistor material, this (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> and Y<sub>2</sub>O<sub>3</sub> as a material for stabilizing the resistivity of the thermistor are used.

In the second preparation step, for the purpose of obtaining the desired resistivity and resistivity temperature coefficient, (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> and Y<sub>2</sub>O<sub>3</sub> are first weighed so that a compounding molar ratio of (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> and Y<sub>2</sub>O<sub>3</sub> becomes 14:86, to make 500 g as the total amount. In the same manner as in Example 1, a sintering auxiliary is added (compounding 2).

Subsequently, (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> + Y<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub> + CaCO<sub>3</sub> as compounded are mixed, ground, granulated, dried, molded and sintered in the same manner as in Example 1 to obtain a thermistor element having Y(Cr<sub>0.5</sub>Mn<sub>0.5</sub>)O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> as an element portion, which is then incorporated into a temperature sensor.

Furthermore, in the above second preparation step, (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> and Y<sub>2</sub>O<sub>3</sub> are weighed so that a compounding molar ratio of (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> and Y<sub>2</sub>O<sub>3</sub> becomes 38:62 and 3:97. Then, a thermistor element is made in the same procedure as described above and is incorporated into a temperature sensor. The respective elements of this Example are referred to as an element No. 4, an element No. 5 and an element No. 6 in the sequence of the compounding molar ratio of (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> and Y<sub>2</sub>O<sub>3</sub>, e.g. 14:86, 38:62 and 3:97.

As described above, in this Example, Y of Y<sub>2</sub>O<sub>3</sub> is incorporated into (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> in case of mixing and sintering and excess oxygen atoms are liberated in the air. As a result, aY(Cr<sub>0.5</sub>Mn<sub>0.5</sub>)O<sub>3</sub> · bY<sub>2</sub>O<sub>3</sub> as a mixed sintered body of perovskite type Y(Cr<sub>0.5</sub>Mn<sub>0.5</sub>)O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> is obtained.

Therefore, the ratio of the molar fraction a:b of aY(Cr<sub>0.5</sub>Mn<sub>0.5</sub>)O<sub>3</sub> · bY<sub>2</sub>O<sub>3</sub> in this Example is slightly larger than a compounding molar ratio of the above (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> and Y<sub>2</sub>O<sub>3</sub>. For example, even if the compounding molar ratio

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is 3:97,  $a \geq 0.05$  and  $b \leq 0.95$ . This fact has already confirmed by the examination of the composition and construction of the mixed sintered body by using SEM, EPMA, etc.

5           Then, the temperature sensors made by incorporating  
the elements No. 4 to No. 6 were put in a high-temperature  
oven and temperature characteristics of the resistivity  
were evaluated within the range from room temperature  
(27°C) to 1000°C in the same manner as in Example 1. The  
10       evaluation results are shown in Table 2.

Table <Example 2>

No.	Raw material composition (mol %)		Resistivity (kΩ )		Resistivity temperature coefficient (K)	Change in resistivity (%)
	(Cr <sub>1.5</sub> Mn <sub>1.5</sub> )O <sub>4</sub>	Y <sub>2</sub> O <sub>3</sub>	Room temperature (27°C)	1000°C		
4	14	86	60	0.15	2350	-7.0
5	38	62	40	0.11	2300	-5.0
6	3	97	100	0.22	2400	-5.0

As shown in Table 2, the wide-range type thermistor element of Example 2 can realize the same effect as that described in Example 1 within the range where the molar fraction ( $a + b = 1$ ) of  $aY(Cr_{0.5}Mn_{0.5})O_3 \cdot bY_2O_3$  satisfy the relations:  $0.05 \leq a < 1$  and  $0 < b \leq 0.95$ .

(Example 3)

In Example 3, a mixed sintered body of  $Y(CrMnTi)O_3$  and  $Y_2O_3$  is obtained from  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$ .  $Y(CrMnTi)O_3$  has a perovskite structure and the composition ratio of each atom is a stoichiometric ratio, e.g.  $Y(Cr_{0.45}Mn_{0.45}Ti_{0.1})O_3$ . The same rule applies correspondingly to the following each  $Y(CrMnTi)O_3$ .

In this Example, since Ti of  $TiO_2$  is incorporated into  $Y(Cr_{0.5}Mn_{0.5})O_3$  in the solid state in case of mixing and sintering, Y is selected as  $M^1$  and Cr, Mn and Ti are selected as  $M^2$  in  $M^1M^2O_3$ .

A flow chart illustrating a production step of the thermistor element of Example 3 is shown in Fig. 6. This production step is roughly divided into a first preparation step from compounding 1 to formation of  $Y(Cr_{0.5}Mn_{0.5})O_3$ , and a second preparation step from compounding (compounding 2) of the resulting  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $TiO_2$  to completion of a thermistor element.

The first preparation step is the same as that of Example 1 and is omitted in this Example. As a wide-range type thermistor material of this Example, this  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  as a material for stabilizing the resistivity of the thermistor and  $TiO_2$  (additive) as a resistance for adjusting the resistivity.

In the second preparation step, for the purpose of obtaining desired resistivity and resistivity temperature coefficient,  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $TiO_2$  are first weighed so that a molar ratio  $Y(Cr_{0.5}Mn_{0.5})O_3:Y_2O_3:TiO_2$  becomes 37:59:4 to make 500 g as the total amount (compounding 1). In the same manner as in Example 1, a sintering auxiliary is added (compounding 2).

Subsequently,  $Y(Cr_{0.5}Mn_{0.5})O_3 + Y_2O_3 + TiO_2 + SiO_2 + CaCO_3$  are compounded, mixed, ground, granulated, dried, molded and fired in the same manner as in Example 1 to obtain a thermistor element having  $Y(CrMnTi)O_3 \cdot Y_2O_3$  as an element portion, which is then incorporated into a temperature sensor.

Furthermore, in the above second preparation step,  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $TiO_2$  are weighed so that a compounding ratio  $Y(Cr_{0.5}Mn_{0.5})O_3:Y_2O_3:TiO_2$  becomes 87:5:8 and 5:94.5:0.5. Then, a thermistor element is made in the same procedure as described above and is incorporated into a temperature sensor. The respective elements of this Example are referred to as an element No. 7, an element No. 8 and an element No. 9 in the sequence of the molar ratio  $Y(Cr_{0.5}Mn_{0.5})O_3:Y_2O_3:TiO_2$ , e.g. 37:59:4, 87:5:8 and 5:94.5:0.5.

The molar fraction (a, b) of  $aY(CrMnTi)O_3 \cdot bY_2O_3$  constituting each element of Example 3 is the same as a ratio of  $Y(Cr_{0.5}Mn_{0.5})O_3:Y_2O_3$  in the compounding ratio. In this connection, a:b ( $a + b = 1$ ) of the element No. 7, that of the element No. 8 and that of the element No. 9 are 0.39:0.61, 0.95:0.05 and 0.05:0.95, respectively.

Then, the temperature sensors made by incorporating the elements No. 7 to No. 9 were put in a high-temperature oven and temperature characteristics of the resistivity were evaluated within the range from room temperature ( $27^\circ C$ ) to  $1000^\circ C$  in the same manner as in Example 1. The evaluation results are shown in Table 3.

Table &lt;Example 3&gt;

No.	Raw material composition (mol %)			Resistivity (k $\Omega$ )		Resistivity temperature coefficient (K)	Change in resistivity (%)
	Y(Cr <sub>0.5</sub> Mn <sub>0.5</sub> )O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Room temperature (27°C)	1000°C		
7	37	59	4	50	0.16	2250	-5.0
8	87	5	8	30	0.10	2240	-4.0
9	5	94.5	0.5	100	0.18	2480	-4.0



As shown in Table 3, the wide-range type thermistor element of Example 3 can realize the same effect as that described in Example 1 within the range where the molar fraction ( $a + b = 1$ ) of  $aY(CrMnTi)O_3 \cdot bY_2O_3$  satisfy the relations:  $0.05 \leq a < 1$  and  $0 < b \leq 0.95$ .

(Example 4)

In Example 4, a mixed sintered body of  $Y(CrMnTi)O_3 \cdot Y_2O_3$  is obtained from  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $YTiO_3$ . In this Example, since Y and Ti of  $YTiO_3$  are incorporated into  $Y(Cr_{0.5}Mn_{0.5})O_3$  in the solid state in case of mixing and sintering, Y is selected as  $M^1$  and Cr, Mn and Ti are selected as  $M^2$  in  $M^1M^2O_3$ .

A flow chart illustrating a production step of the thermistor element of Example 4 is shown in Fig. 7. This production step is roughly divided into a first preparation step from compounding 1 to formation of  $Y(Cr_{0.5}Mn_{0.5})O_3$ , a second preparation step from compounding (compounding 2) of the resulting  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $YTiO_3$  to completion of a thermistor element and a third preparation step of obtaining  $YTiO_3$  to be fed to the second preparation step (from compounding 3 to  $YTiO_3$  in the figure).

The first preparation step is the same as that of Example 1 and is also omitted in this Example. In the third preparation step,  $Y_2O_3$  and  $TiO_2$  (purity of all components is not less than 99.9%) are first prepared and then weighed so that a molar ratio of Y:Ti becomes 1:1 to make 500 g as the total amount (compounding 3).

Using a resin pot (volume: 5 liter) containing  $Al_2O_3$  or  $ZrO_2$  pebbles having a diameter of 15  $\phi$  (2.5 kg) and pebbles having a diameter of 20  $\phi$  (2.5 kg) as a ball mill to mix these weighed substances, the total amount of  $Y_2O_3$  and  $TiO_2$  is charged in the pot, in order to mix these weighed substances. After adding 1500 cc of purified water, the mixture was mixed at 60 rpm for 6 hours (mixing step).

A mixed slurry of  $Y_2O_3$  and  $TiO_2$  obtained after a

mixing treatment is transferred to a porcelain evaporating dish, and then dried by using a hot-air dryer at 150°C for 12 hours or more to obtain a mixed solid of  $Y_2O_3$  and  $TiO_2$ . Subsequently, this mixed solid is roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a mixed powder of  $Y_2O_3$  and  $TiO_2$ .

In the calcination step, this mixed powder is charged in a crucible made of 99.3%  $Al_2O_3$  and then calcined in a high-temperature oven in the air at 1100 to 1300°C for 1 to 2 hours to obtain  $YTiO_3$ .  $YTiO_3$  as a bulk solid obtained in the calcination was roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a powder.

As a wide-range type thermistor material of this Example,  $Y(Cr_{0.5}Mn_{0.5})O_3$  obtained in the first preparation step,  $Y_2O_3$  and  $YTiO_3$  (additive) are used.

In the second preparation step, for the purpose of obtaining desired resistivity and resistivity temperature coefficient,  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $YTiO_3$  are first weighed so that a compounding molar ratio  $Y(Cr_{0.5}Mn_{0.5})O_3:Y_2O_3:YTiO_3$  becomes 37:60:3 to make 500 g as the total amount (compounding 1). In the same manner as in Example 1, a sintering auxiliary is added (compounding 2).

Subsequently,  $Y(Cr_{0.5}Mn_{0.5})O_3 + Y_2O_3 + YTiO_3 + SiO_2 + CaCO_3$  are compounded, mixed, ground, granulated, dried, molded and fired in the same manner as in Example 1 to obtain a thermistor element having  $Y(CrMnTi)O_3 \cdot Y_2O_3$  as an element portion, which is then incorporated into a temperature sensor.

Furthermore, in the above second preparation step,  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $YTiO_3$  are weighed so that a compounding ratio of  $Y(Cr_{0.5}Mn_{0.5})O_3:Y_2O_3:YTiO_3$  becomes 87:6:3 and 5:94.7:0.3. Then, a thermistor element is made in the same procedure as described above and is incorporated into a temperature sensor. The respective elements of this Example are referred to as an element No.

In each element of Example 4, since incorporation of Y and Ti of  $\text{YTiO}_3$  in the solid state arises, as described above, the molar fraction (a, b) of  $a\text{Y}(\text{CrMnTi})\text{O}_3 \cdot b\text{Y}_2\text{O}_3$  in each element is slightly larger than a ratio of  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3:\text{Y}_2\text{O}_3$  in the compounding molar ratio, but is almost the same.

Then, the temperature sensors made by incorporating the elements No. 10 to No. 12 were put in a high-temperature oven and temperature characteristics of the resistivity were evaluated within the range from room temperature ( $27^\circ\text{C}$ ) to  $1000^\circ\text{C}$  in the same manner as in Example 1. The evaluation results are shown in Table 4.

Table <Example 4>

No.	Raw material composition (mol %)			Resistivity (k $\Omega$ )		Resistivity temperature coefficient (K)	Change in resistivity (%)
	Y(Cr <sub>0.5</sub> Mn <sub>0.5</sub> )O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	YTiO <sub>3</sub>	Room temperature (27°C)	1000°C		
10	37	60	3	50	0.17	2230	-5.0
11	87	6	3	30	0.11	2200	-4.0
12	5	94.7	0.3	100	0.20	2440	-4.0

As shown in Table 4, the wide-range type thermistor element of Example 4 can realize the same effect as that described in Example 1 within the range where the molar fraction ( $a + b = 1$ ) of  $aY(CrMnTi)O_3 \cdot bY_2O_3$  satisfy the relations:  $0.05 \leq a < 1$  and  $0 < b \leq 0.95$ .

(Example 5)

In Example 5, a mixed sintered body of  $Y(CrMnTi)O_3 \cdot Y_2O_3$  is obtained from  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $TiO_2$ . In this Example, since Y of  $Y_2O_3$  and Ti of  $TiO_2$  are incorporated into  $(Mn_{1.5}Cr_{1.5})O_4$  in the solid state in case of mixing and sintering, Y is selected as  $M^1$  and Cr, Mn and Ti are selected as  $M^2$  in  $M^1M^2O_3$ .

A flow chart illustrating a production step of the thermistor element of Example 5 is shown in Fig. 8. This production step is roughly divided into a first preparation step from compounding 1 to formation of  $(Mn_{1.5}Cr_{1.5})O_4$  and a second preparation step from compounding (compounding 2) of the resulting  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $TiO_2$  to completion of a thermistor element.

The first preparation step is the same as that of Example 2 and is omitted in this Example. As a wide-range type thermistor material of this Example, the above  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $TiO_2$  (additive) are used.

In the second preparation step, for the purpose of obtaining desired resistivity and resistivity temperature coefficient,  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $TiO_2$  are first weighed so that a compounding molar ratio of  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $TiO_2$  becomes 12:84:4, to make 500 g as the total amount. In the same manner as in Example 1, a sintering auxiliary is added (compounding 2).

Subsequently,  $(Mn_{1.5}Cr_{1.5})O_4 + Y_2O_3 + TiO_2 + SiO_2 + CaCO_3$  are compounded, mixed, ground, granulated, dried, molded and calcined in the same manner as in Example 1 to obtain a thermistor element having  $Y(CrMnTi)O_3 \cdot Y_2O_3$  as an element portion, which is then incorporated into a temperature sensor.

Furthermore, in the above second preparation step,

(Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub>, Y<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are weighed so that a  
compounding molar ratio of (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub>, Y<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>  
becomes 36:61:3 and 4:95.7:0.3. Then, a thermistor  
element is made in the same procedure as described above  
5 and is incorporated into a temperature sensor. The  
respective elements of Example 5 are referred to as an  
element No. 13, an element No. 14 and an element No. 15 in  
the sequence of the compounding molar ratio  
(Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub>:Y<sub>2</sub>O<sub>3</sub>: TiO<sub>2</sub>, e.g. 12:84:4, 36:61:3 and  
10 4:95.7:0.3.

As described above, in Example 5, Y of Y<sub>2</sub>O<sub>3</sub> and Ti of  
TiO<sub>2</sub> are incorporated into (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub> in the solid state  
in case of mixing and sintering and excess oxygen atoms  
are liberated in the air. As a result, aY(CrMnTi)O<sub>3</sub>·bY<sub>2</sub>O<sub>3</sub>  
15 as a mixed sintered body of perovskite type Y(CrMnTi)O<sub>3</sub> and  
Y<sub>2</sub>O<sub>3</sub>.

Therefore, the ratio of the molar fraction a:b of  
aY(CrMnTi)O<sub>3</sub>·bY<sub>2</sub>O<sub>3</sub> in Example 5 is slightly larger than a  
compounding molar ratio of the above (Mn<sub>1.5</sub>Cr<sub>1.5</sub>)O<sub>4</sub>:Y<sub>2</sub>O<sub>3</sub>.  
20 For example, even if the compounding molar ratio is  
4:95.7,  $a \geq 0.05$  and  $b \leq 0.95$ . This fact has already  
confirmed by the examination of the composition and  
construction of the mixed sintered body by using SEM,  
EPMA, etc.

25 Then, the temperature sensors made by incorporating  
the elements No. 13 to No. 15 were put in a high-  
temperature oven and temperature characteristics of the  
resistivity were evaluated within the range from room  
temperature (27°C) to 1000°C in the same manner as in  
30 Example 1. The evaluation results are shown in Table 5.

Table <Example 5>

No.	Raw material composition (mol %)			Resistivity (k $\Omega$ )		Resistivity temperature coefficient (K)	Change in resistivity (%)
	(Cr <sub>1.5</sub> Mn <sub>1.5</sub> )O <sub>4</sub>	Y <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Room temperature (27°C)	1000°C		
13	12	84	4	60	0.15	2350	-5.0
14	36	61	3	40	0.11	2300	-4.0
15	4	95.7	0.3	100	0.22	2400	-4.0

As shown in Table 5, the wide-range type thermistor element of Example 5 can realize the same effect as that described in Example 1 within the range where the molar fraction ( $a + b = 1$ ) of  $aY(CrMnTi)O_3 \cdot bY_2O_3$  satisfy the relations:  $0.05 \leq a < 1$  and  $0 < b \leq 0.95$ .

(Example 6)

In Example 6, a mixed sintered body of  $Y(CrMnTi)O_3 \cdot Y_2O_3$  is obtained from  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $YTiO_3$ . In this Example, since Y and Ti of  $YTiO_3$  are incorporated into  $(Mn_{1.5}Cr_{1.5})O_4$  in the solid state in case of mixing and sintering, Y is selected as  $M^1$  and Cr, Mn and Ti are selected as  $M^2$  in  $M^1M^2O_3$ .

A flow chart illustrating a production step of the thermistor element of Example 6 is shown in Fig. 14. This production step is roughly divided into a first preparation step from compounding 1 to formation of  $(Mn_{1.5}Cr_{1.5})O_4$ , a second preparation step from compounding (compounding 2) of the resulting  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $YTiO_3$  to completion of a thermistor element and a third preparation step of obtaining  $YTiO_3$  to be fed to the second preparation step (from compounding 3 to  $YTiO_3$  in the figure).

The first preparation step is the same as that of Example 2 and is omitted in this Example. As a wide-range type thermistor material of this Example,  $(Mn_{1.5}Cr_{1.5})O_4$  obtained in the first preparation step,  $Y_2O_3$  and  $YTiO_3$  (additive) obtained in the third preparation step are used.

In the second preparation step, for the purpose of obtaining desired resistivity and resistivity temperature coefficient,  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $YTiO_3$  are first weighed so that a compounding molar ratio of  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $YTiO_3$  becomes 13:84:3, to make 500 g as the total amount. In the same manner as in Example 1, a sintering auxiliary is added (compounding 2).

Subsequently,  $(Mn_{1.5}Cr_{1.5})O_4 + Y_2O_3 + YTiO_3 + SiO_2 + CaCO_3$  are compounded, mixed, ground, granulated, dried,

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molded and calcined in the same manner as in Example 1 to obtain a thermistor element having  $Y(CrMnTi)O_3 \cdot Y_2O_3$  as an element portion, which is then incorporated into a temperature sensor.

5           Furthermore, in the above second preparation step,  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $YTiO_3$  are weighed so that a compounding molar ratio of  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $YTiO_3$  becomes 37:61:2 and 4:95.8:0.2. Then, a thermistor element is made in the same procedure as described above  
10 and is incorporated into a temperature sensor.

          The respective elements of Example 6 are referred to as an element No. 16, an element No. 17 and an element No. 18 in the sequence of the compounding molar ratio of  $Y(Cr_{1.5}Mn_{1.5})O_4:Y_2O_3:YTiO_3$ , e.g. 13:84:3, 37:61:2 and  
15 4:95.8:0.2.

          As described above, in Example 6, Y of  $Y_2O_3$  and Ti of  $YTiO_3$  are incorporated into  $(Mn_{1.5}Cr_{1.5})O_4$  in the solid state in case of mixing and sintering and excess oxygen atoms are liberated into the air. As a result,  
20  $aY(CrMnTi)O_3 \cdot bY_2O_3$  as a mixed sintered body of a perovskite type  $Y(CrMnTi)O_3$  and  $Y_2O_3$ .

          Therefore, the ratio of the molar fraction a:b of  $aY(CrMnTi)O_3 \cdot bY_2O_3$  in Example 6 is slightly larger than a compounding molar ratio of the above  $(Mn_{1.5}Cr_{1.5})O_4:Y_2O_3$ .  
25 For example, even if the compounding molar ratio is 4:95.8,  $a \geq 0.05$  and  $b \leq 0.95$ . This fact has already confirmed by the examination of the composition and construction of the mixed sintered body by using SEM, EPMA, etc.

30           Then, the temperature sensors made by incorporating the elements No. 16 to No. 18 were put in a high-temperature oven and temperature characteristics of the resistivity were evaluated within the range from room temperature (27°C) to 1000°C in the same manner as in  
35 Example 1. The evaluation results are shown in Table 6.

Table <Example 6>

No.	Raw material composition (mol %)			Resistivity (k $\Omega$ )		Resistivity temperature coefficient (K)	Change in resistivity (%)
	(Cr <sub>1.5</sub> Mn <sub>1.5</sub> )O <sub>4</sub>	Y <sub>2</sub> O <sub>3</sub>	YTiO <sub>3</sub>	Room temperature (27°C)	1000°C		
16	13	84	3	58	0.15	2340	-5.0
17	37	61	2	35	0.11	2260	-4.0
18	4	95.8	0.2	100	0.20	2440	-4.0

As shown in Table 6, the wide-range type thermistor element of Example 6 can realize the same effect as that described in Example 1 within the range where the molar fraction ( $a + b = 1$ ) of  $aY(CrMnTi)O_3 \cdot bY_2O_3$  satisfy the relations:  $0.05 \leq a < 1$  and  $0 < b \leq 0.95$ .

(Comparative Example 1)

As Comparative Example 1, a temperature sensor using a thermistor element having the composition of  $Y(Cr_{0.5}Mn_{0.5})O_3$  alone without using  $Y_2O_3$  for stabilizing the resistivity will be described.

In the same manner as in Example 1,  $Y(Cr_{0.5}Mn_{0.5})O_3$  is obtained. A temperature sensor using  $Y(Cr_{0.5}Mn_{0.5})O_3$  prepared as a raw material was evaluated. The results are shown in Table 7. The resistivity characteristics were evaluated in the same manner as in Example 1.

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Table <Example 7>

Composition of element portion	Resistivity (k $\Omega$ )		Resistivity temperature coefficient (K)	Change in resistivity (%)	
	Room temperature (27°C)	1000°C			
Y(Cr <sub>0.5</sub> Mn <sub>0.5</sub> )O <sub>3</sub>	10	0.05	2080	-20.0	Comparative Example 1
YTiO <sub>3</sub>	>1000	0.2	12200	-40.0	Comparative Example 2

As is apparent from Table 7, in case that  $Y_2O_3$  for stabilizing the resistivity is not used, the resistivity at high temperature range (e.g.  $1000^{\circ}C$ , etc.) is too low and, therefore, the temperature cannot be detected. As is also apparent from the results of the high-temperature durability test (change in resistivity), the change in resistivity  $\Delta R$  exceeds  $\pm 20\%$  and, therefore, a wide-range thermistor element having stable characteristics can not be provided.

Accordingly, the thermistor element having the composition of  $Y(Cr_{0.5}Mn_{0.5})O_3$  alone in Comparative Example 1 cannot be used as the element of the desired temperature sensor of the present invention.

(Comparative Example 2)

As Comparative Example 2, a temperature sensor using a thermistor element having the composition of  $YTiO_3$  alone without using  $Y_2O_3$  for stabilizing the resistivity will be described.

In the same manner as in Example 4,  $YTiO_3$  is obtained. A temperature sensor using  $YTiO_3$  prepared as a raw material was evaluated. The results are shown in Table 7. The resistivity characteristics were evaluated in the same manner as in Example 1.

As is apparent from Table 7, in the thermistor element having the composition of  $YTiO_3$  alone, the resistivity at low temperature range (e.g.  $27^{\circ}C$ , etc.) is remarkably large (e.g.  $1000\ k\Omega$  or more), etc.) and, therefore, the temperature cannot be detected. As is also apparent from the results of the high-temperature durability test, the change in resistivity  $\Delta R$  exceeds  $\pm 20\%$  and, therefore, a wide-range thermistor element having stable characteristics cannot be provided.

Accordingly, the thermistor element having the composition of  $YTiO_3$  alone can not be used as the element of the desired temperature sensor of the present invention.

(Example 7)

In Example 7, as the raw material for obtaining a

mixed sintered body ( $M^1 = Y$ ,  $M^2 = Cr$ ,  $Mn$ ) of  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$ ,  $Y(Cr_{0.5}Mn_{0.5})O_3$  is first prepared. A flow chart illustrating a production step of the thermistor element of Example 7 is shown in Fig. 10. This Example relates to  
5 a production method according to the above second aspect.

As the starting material,  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$ , high purity (99.9%) raw materials are used. The average particle diameter of  $Y_2O_3$ , that of  $Cr_2O_3$  and that of  $Mn_2O_3$  are  $1.0 \mu m$ ,  $2.0$  to  $4.0 \mu m$  and  $7.0$  to  $15.0 \mu m$ ,  
10 respectively. The average particle diameters of the respective raw materials were the same as those in the following Examples 8 to 20 as well as Comparative Examples 1 and 2.

In the first preparation step (from compounding 1 to  $Y(Cr_{0.5}Mn_{0.5})O_3$  in the figure),  $Y_2O_3$  (268.8 g),  $Cr_2O_3$  (101 g) and  $Mn_2O_3$  (104 g) are weighed so that a molar ratio (Y:Cr:Mn) becomes 2:1:1 (compounding 1).  
15

Using a resin pot (volume: 5 liter) containing  $Al_2O_3$  or  $ZrO_2$  pebbles having a diameter of  $15 \phi$  (2.5 kg) and  
20 pebbles having a diameter of  $20 \phi$  (2.5 kg) as a ball mill to mix these weighed substances,  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  are charged in the pot, in order to mix these weighed substances. After adding 1500 cc of purified water, the mixture was mixed at 60 rpm for 4 hour (mixing step).

25 A mixed slurry of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  obtained after a mixing treatment is transferred to a porcelain evaporating dish, and then dried by using a hot-air dryer at  $100$  to  $150^\circ C$  for 12 to 17 hours to obtain a mixed solid of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$ . Subsequently, this mixed solid is  
30 roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a mixed powder of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$ .

In the temporary calcination step, the mixed powder of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  is charged in a crucible made of  
35 99.3%  $Al_2O_3$  and then heat-treated in a high-temperature oven in an atmosphere under a normal pressure at  $1100^\circ C$  for 2 hours to obtain  $Y(Cr_{0.5}Mn_{0.5})O_3$ .  $Y(Cr_{0.5}Mn_{0.5})O_3$  as a



Variable	Mean	SD	Min	Max
Age	34.5	10.2	22	55
Gender	0.5	0.5	0	1
Marital status	0.6	0.5	0	1
Education	12.5	1.5	10	15
Income	1500	500	1000	2500
Health status	0.8	0.2	0	1
Employment status	0.7	0.3	0	1
Family size	3.2	1.1	1	5
Home ownership	0.9	0.1	0	1
Vehicle ownership	0.6	0.5	0	1
Internet usage	0.4	0.4	0	1
Smartphone usage	0.8	0.2	0	1
Travel frequency	0.3	0.3	0	1
Exercise frequency	0.2	0.2	0	1
Stress level	0.5	0.3	0	1
Life satisfaction	0.7	0.2	0	1
Community involvement	0.3	0.3	0	1
Volunteering frequency	0.1	0.1	0	1
Political participation	0.2	0.2	0	1
Environmental awareness	0.6	0.2	0	1
Waste recycling frequency	0.4	0.4	0	1
Energy conservation practices	0.5	0.3	0	1
Water conservation practices	0.6	0.2	0	1
Green building practices	0.3	0.3	0	1
Local food consumption	0.2	0.2	0	1
Organic food consumption	0.1	0.1	0	1
Plant-based diet consumption	0.3	0.3	0	1
Reduced meat consumption	0.4	0.4	0	1
Reduced dairy consumption	0.2	0.2	0	1
Reduced egg consumption	0.1	0.1	0	1
Reduced sugar consumption	0.3	0.3	0	1
Reduced salt consumption	0.2	0.2	0	1
Reduced alcohol consumption	0.1	0.1	0	1
Reduced tobacco consumption	0.1	0.1	0	1
Reduced fast food consumption	0.2	0.2	0	1
Reduced processed food consumption	0.1	0.1	0	1
Reduced packaged food consumption	0.2	0.2	0	1
Reduced convenience food consumption	0.1	0.1	0	1
Reduced frozen food consumption	0.1	0.1	0	1
Reduced canned food consumption	0.1	0.1	0	1
Reduced bottled water consumption	0.1	0.1	0	1
Reduced plastic bottle consumption	0.1	0.1	0	1
Reduced paper cup consumption	0.1	0.1	0	1
Reduced paper plate consumption	0.1	0.1	0	1
Reduced paper napkin consumption	0.1	0.1	0	1
Reduced paper towel consumption	0.1	0.1	0	1
Reduced paper bag consumption	0.1	0.1	0	1
Reduced paper cup consumption	0.1	0.1	0	1
Reduced paper plate consumption	0.1	0.1	0	1
Reduced paper napkin consumption	0.1	0.1	0	1
Reduced paper towel consumption	0.1	0.1	0	1
Reduced paper bag consumption	0.1	0.1	0	1
Reduced paper cup consumption	0.1	0.1	0	1
Reduced paper plate consumption	0.1	0.1	0	1
Reduced paper napkin consumption	0.1	0.1	0	1
Reduced paper towel consumption	0.1	0.1	0	1
Reduced paper bag consumption	0.1	0.1	0	1
Reduced paper cup consumption	0.1	0.1	0	1
Reduced paper plate consumption	0.1	0.1	0	1
Reduced paper napkin consumption	0.1	0.1	0	1
Reduced paper towel consumption	0.1	0.1	0	1
Reduced paper bag consumption	0.1	0.1	0	1
Reduced paper cup consumption	0.1	0.1	0	1
Reduced paper plate consumption	0.1	0.1	0	1
Reduced paper napkin consumption	0.1	0.1	0	1
Reduced paper towel consumption	0.1	0.1	0	1
Reduced paper bag consumption	0.1	0.1	0	1
Reduced paper cup consumption	0.1	0.1	0	1
Reduced paper plate consumption	0.1	0.1	0	1
Reduced paper napkin consumption	0.1	0.1	0	1
Reduced paper towel consumption	0.1	0.1	0	1
Reduced paper bag consumption	0.1	0.1	0	1
Reduced paper cup consumption	0.1	0.1	0	1
Reduced paper plate consumption	0.1	0.1	0	1
Reduced paper napkin consumption	0.1	0.1	0	1
Reduced paper towel consumption	0.1	0.1	0	1
Reduced paper bag consumption	0.1	0.1	0	1
Reduced paper cup consumption	0.1	0.1	0	1
Reduced paper plate consumption	0.1	0.1	0	1
Reduced paper napkin consumption	0.1	0.1	0	1
Reduced paper towel consumption	0.1	0.1	0	1
Reduced paper bag consumption	0.1	0.1	0	1

[illegible]

Variable	Mean	SD	Min	Max
Age	34.5	10.2	22	55
Gender	0.5	0.5	0	1
Marital status	0.6	0.5	0	1
Education	12.5	1.5	10	15
Income	1500	500	1000	2500
Health status	0.8	0.2	0	1
Stress level	3.5	1.5	1	5
Life satisfaction	4.2	1.0	3	5
Work-life balance	3.8	1.2	2	5
Family support	4.5	1.0	3	5
Community support	4.0	1.0	3	5
Healthcare access	4.3	1.0	3	5
Quality of life	4.1	1.0	3	5
Overall well-being	4.0	1.0	3	5

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Variable	Mean	SD	Min	Max
Age	34.5	10.2	22	55
Gender	0.5	0.5	0	1
Marital status	0.6	0.5	0	1
Education	12.5	1.5	10	15
Income	1500	500	1000	2500
Health status	0.8	0.2	0	1
Employment status	0.7	0.3	0	1
Life satisfaction	4.5	1.0	3	6
Depression	0.2	0.4	0	1
Stress	3.5	1.5	2	5
Resilience	4.0	1.0	3	5
Optimism	4.2	1.0	3	5
Gratitude	4.8	1.0	3	5
Forgiveness	4.5	1.0	3	5
Self-esteem	4.0	1.0	3	5
Life purpose	4.5	1.0	3	5
Meaning in life	4.2	1.0	3	5
Existential well-being	4.0	1.0	3	5
Overall well-being	4.5	1.0	3	5



Table <Example 8>

	Raw material component in case of grinding	Average particle diameter after grinding ( $\mu$ m)	Temperature accuracy ( $^{\circ}$ C)
Example 7	Y(CrMn)O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub>	0.4	$\pm 10$
Example 8	(Mn <sub>1.5</sub> Cr <sub>1.5</sub> )O <sub>4</sub> , Y <sub>2</sub> O <sub>3</sub>	0.5	$\pm 10$
Example 9	Y(CrMn)O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub>	0.4	$\pm 8.0$
Example 10	(Mn <sub>1.5</sub> Cr <sub>1.5</sub> )O <sub>4</sub> , Y <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub>	0.5	$\pm 8.0$
Example 11	Y(CrMn)O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub>	2.7	$\pm 25$
Example 12	(Mn <sub>1.5</sub> Cr <sub>1.5</sub> )O <sub>4</sub> , Y <sub>2</sub> O <sub>3</sub>	2.7	$\pm 30$
Example 13	Y(CrMn)O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub>	3.0	$\pm 25$
Example 14	(Mn <sub>1.5</sub> Cr <sub>1.5</sub> )O <sub>4</sub> , Y <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub>	3.0	$\pm 25$

In Table 8,  $Y(CrMn)O_3$  represents  $Y(Cr_{0.5}Mn_{0.5})O_3$ . The raw material component in case of grinding represents a raw material component in the grinding step of the second preparation step ( $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$  in this Example) and the average particle diameter ( $\mu m$ ) after grinding represents an average particle diameter of a raw slurry after grinding of the second preparation step ( $0.4 \mu m$  in this Example). The same rule applies correspondingly to the following Examples 8 to 14.

Regarding the temperature sensor of Example 7, a temperature accuracy of  $\pm 10^\circ C$  can be obtained.

As described in the above second aspect, the evaluation method of the temperature accuracy is as follows.

That is, a standard deviation  $\sigma$  (sigma) of the resistivity at  $350^\circ C$  is calculated from resistivity-temperature data of 100 temperature sensors. Using  $6\sigma$  (standard deviation) as a scatter width (two sides), a value A obtained by dividing the value, calculated by this scatter width of the resistivity based on the temperature, by 2 is represented as "temperature accuracy  $\pm A^\circ C$ " and the accuracy is evaluated.

(Example 8)

In Example 8, as the raw material for obtaining a mixed sintered body ( $M^1 = Y$ ,  $M^2 = Cr$ ,  $Mn$ ) of  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$ ,  $(Mn_{1.5}Cr_{1.5})O_4$  obtained by calcining a mixture of an oxide of Cr and an oxide of Mn at  $1000^\circ C$  or more is first prepared. A flow chart illustrating a production step of the thermistor element of Example 8 is shown in Fig. 11. This Example relates to a production method according to the above second embodiment.

In the first preparation step (from compounding 1 to  $(Mn_{1.5}Cr_{1.5})O_4$  in the figure),  $Cr_2O_3$  (101 g) and  $Mn_2O_3$  (104 g) are weighed so that a molar ratio (Cr:Mn) becomes 1:1 (compounding 1).

These  $Cr_2O_3$  and  $Mn_2O_3$  are mixed (6 hours), dried, ground and heat-treated in the same manner as in Example 7

to obtain  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$ .  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  as a bulk solid obtained by the heat treatment was roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a powder.

5           The above  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  and  $\text{Y}_2\text{O}_3$  are used as the thermistor material.

          In the second preparation step (starting from compounding 2 in the figure), for the purpose of obtaining the desired resistivity and resistivity temperature  
10       coefficient,  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  (average particle diameter: 2 to 5  $\mu\text{m}$ , 630 g) and  $\text{Y}_2\text{O}_3$  (average particle diameter: 1.0  $\mu\text{m}$ , 1370 g) are first weighed so that a compounding molar ratio of  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4:\text{Y}_2\text{O}_3$  becomes 100:216, to make 2000 g as the total amount. In the same manner as in Example 7,  
15        $\text{SiO}_2$  (60 g) and  $\text{CaCO}_3$  (90 g) are added as a sintering auxiliary (compounding 2).

          In order to perform atomization of the thermistor material, a pearl mill device is used in the same manner as in Example 7. The raw slurry of the thermistor  
20       material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was 0.5  $\mu\text{m}$ . This average particle diameter is smaller than the average particle diameter (1.0  $\mu\text{m}$ ) of  $\text{Y}_2\text{O}_3$  before mixing.

25           The raw slurry of the resulting thermistor material is granulated and dried to obtain a granulated powder of the thermistor material. The grinding conditions of the pearl mill device and drying conditions of the spray drier are the same as those of Example 7.

30           The molding is performed by the molding method in the same manner as in Example 7 to obtain a thermistor element, which is incorporated into a temperature sensor assay to give a temperature sensor.

          The evaluation results are shown in Table 8.  
35       Regarding the temperature sensor of Example 8, a temperature accuracy of  $\pm 10^\circ\text{C}$  can be obtained. The

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Microclimate		Soil		Plant		Insect		Fungal		Bacterial		Viral		Protozoan		Other			
Parameter	Unit	Parameter	Unit	Parameter	Unit	Parameter	Unit	Parameter	Unit	Parameter	Unit	Parameter	Unit	Parameter	Unit	Parameter	Unit		
Temperature	°C	Moisture	%	Height	m	Length	mm	Spore count	10 <sup>6</sup>	Spore count	10 <sup>6</sup>	Spore count	10 <sup>6</sup>	Spore count	10 <sup>6</sup>	Spore count	10 <sup>6</sup>	Spore count	10 <sup>6</sup>
Humidity	%	pH		Width	mm	Weight	g	Germination %	%	Germination %	%	Germination %	%	Germination %	%	Germination %	%	Germination %	%
Light intensity	μmol/m <sup>2</sup> /s	EC	dS/m	Area	cm <sup>2</sup>	Volume	ml	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
CO <sub>2</sub> concentration	ppm	Organic matter	%	Stem diameter	mm	Stem diameter	mm	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
NO <sub>2</sub> concentration	ppm	Nitrogen	mg/kg	Leaf area	cm <sup>2</sup>	Leaf area	cm <sup>2</sup>	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
NO <sub>3</sub> concentration	ppm	Phosphorus	mg/kg	Stomatal conductance	mol/m <sup>2</sup> /s	Stomatal conductance	mol/m <sup>2</sup> /s	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
SO <sub>2</sub> concentration	ppm	Potassium	mg/kg	Transpiration rate	mmol/m <sup>2</sup> /s	Transpiration rate	mmol/m <sup>2</sup> /s	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
O <sub>3</sub> concentration	ppm	Sulfur	mg/kg	Chlorophyll content	mg/g	Chlorophyll content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>10</sub> concentration	μg/m <sup>3</sup>	Copper	mg/kg	Carotenoid content	mg/g	Carotenoid content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>2.5</sub> concentration	μg/m <sup>3</sup>	Zinc	mg/kg	Protein content	mg/g	Protein content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>10-2.5</sub> concentration	μg/m <sup>3</sup>	Iron	mg/kg	Starch content	mg/g	Starch content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>2.5-10</sub> concentration	μg/m <sup>3</sup>	Manganese	mg/kg	Cellulose content	mg/g	Cellulose content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>10-2.5-10</sub> concentration	μg/m <sup>3</sup>	Chromium	mg/kg	Lignin content	mg/g	Lignin content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>2.5-10-10</sub> concentration	μg/m <sup>3</sup>	Nickel	mg/kg	Cellulose content	mg/g	Cellulose content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>10-2.5-10-10</sub> concentration	μg/m <sup>3</sup>	Cadmium	mg/kg	Cellulose content	mg/g	Cellulose content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>2.5-10-10-10</sub> concentration	μg/m <sup>3</sup>	Lead	mg/kg	Cellulose content	mg/g	Cellulose content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>10-2.5-10-10-10</sub> concentration	μg/m <sup>3</sup>	Barium	mg/kg	Cellulose content	mg/g	Cellulose content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>2.5-10-10-10-10</sub> concentration	μg/m <sup>3</sup>	Selenium	mg/kg	Cellulose content	mg/g	Cellulose content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>10-2.5-10-10-10-10</sub> concentration	μg/m <sup>3</sup>	Vanadium	mg/kg	Cellulose content	mg/g	Cellulose content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>2.5-10-10-10-10-10</sub> concentration	μg/m <sup>3</sup>	Cobalt	mg/kg	Cellulose content	mg/g	Cellulose content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %	%
PM <sub>10-2.5-10-10-10-10-10</sub> concentration	μg/m <sup>3</sup>	Molybdenum	mg/kg	Cellulose content	mg/g	Cellulose content	mg/g	Survival %	%	Survival %	%	Survival %	%	Survival %	%	Survival %			

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The raw slurry of the resulting thermistor material is granulated and dried to obtain a granulated powder of the thermistor material. The grinding conditions of the pearl mill device and drying conditions of the spray drier are the same as those of Example 7.

The molding is performed by the molding method in the same manner as in Example 7 to obtain a thermistor element, which is incorporated into a typical temperature sensor assay to give a temperature sensor.

The evaluation results are shown in Table 8. Regarding the temperature sensor of Example 9, a temperature accuracy of  $\pm 8^\circ\text{C}$  can be obtained. The evaluation method of the temperature accuracy is the same as that of Example 7.

(Example 10)

In Example 10, as the raw material for obtaining a mixed sintered body ( $M^1 = \text{Y}$ ,  $M^2 = \text{Cr}$ ,  $\text{Mn}$ ,  $\text{Ti}$ ) of  $\text{Y}(\text{CrMnTi})\text{O}_3$  and  $\text{Y}_2\text{O}_3$  from  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$ ,  $\text{Y}_2\text{O}_3$  and  $\text{TiO}_2$ ,  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  obtained by calcining a mixture of an oxide of Cr and an oxide of Mn at  $1000^\circ\text{C}$  or more is first prepared. A flow chart illustrating a production step of the thermistor element of Example 10 is shown in Fig. 13. This Example relates to a production method according to the above second embodiment.

In the first preparation step,  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  is obtained in the same manner as in Example 8.

The above  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$ ,  $\text{Y}_2\text{O}_3$  and  $\text{TiO}_2$  are used as the thermistor material.

In the second preparation step (starting from compounding 2 in the figure), for the purpose of obtaining desired resistivity and resistivity temperature coefficient,  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  (average particle diameter: 2 to  $5 \mu\text{m}$ , 578 g),  $\text{Y}_2\text{O}_3$  (average particle diameter:  $1.0 \mu\text{m}$ , 1355 g) and  $\text{TiO}_2$  (67 g) are first weighed so that a compounding molar ratio  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4:\text{Y}_2\text{O}_3:\text{TiO}_2$  becomes 30:70:10, to make 2000 g as the total amount. In the same

manner as in Example 7,  $\text{SiO}_2$  (60 g) and  $\text{CaCO}_3$  (90 g) are added as a sintering auxiliary (compounding 2).

Then, in order to perform atomization of the thermistor material, a pearl mill device is used as a medium stirring mill. The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was  $0.5 \mu\text{m}$  (micrometer). This average particle diameter is smaller than the average particle diameter  $1.0 \mu\text{m}$  of  $\text{Y}_2\text{O}_3$  before mixing.

The raw slurry of the resulting thermistor material is granulated and dried to obtain a granulated powder of the thermistor material. The grinding conditions of the pearl mill device and drying conditions of the spray drier are the same as those of Example 7.

The molding is performed by the molding method in the same manner as in Example 7 to obtain a thermistor element, which is incorporated into a typical temperature sensor assay to give a temperature sensor.

The evaluation results are shown in Table 8. Regarding the temperature sensor of Example 8, a temperature accuracy of  $\pm 8^\circ\text{C}$  can be obtained. The evaluation method of the temperature accuracy is the same as that of Example 7.

(Example 11)

A flow chart illustrating a production step of the thermistor element of Example 11 is shown in Fig. 14. Regarding Examples 11 to 14, the mixing and grinding are performed by using a ball mill as a conventional method for comparison with Examples 7 to 10 wherein the mixing and grinding (grinding step) in the second preparation step are performed by using a medium stirring mill.

Regarding Example 11, a ball mill as a conventional method is used in the grinding step in the second preparation step of Example 7. In the first preparation step,  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$  is obtained in the same manner as in the first preparation step of Example 7.

In the second preparation step, for the purpose of obtaining desired resistivity and resistivity temperature coefficient,  $Y(Cr_{0.5}Mn_{0.5})O_3$  (average particle diameter: 2 to 5  $\mu m$ , 390 g) and  $Y_2O_3$  (average particle diameter: 1.0  $\mu m$ , 110 g) are first weighed to make 500 g as the total amount. In addition,  $SiO_2$  and  $CaCO_3$  are used as a sintering auxiliary, and  $SiO_2$  (15 g) and  $CaCO_3$  (23 g) are added (compounding 2). Accordingly, 538 g of the total of  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$ ,  $SiO_2$  and  $CaCO_3$  is used as the mixing/grinding raw material.

Regarding the operation conditions of the mixing and grinding, the thermistor raw material is charged in a resin pot (volume: 5 liter) containing  $Al_2O_3$  pebbles having a diameter of 15  $\phi$  (2.5 kg) and pebbles having a diameter of 20  $\phi$  (2.5 kg) and, after adding 1800 cc of purified water, the mixture was mixed and ground at 60 rpm for 6 hours.

The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was 3.0  $\mu m$  (micron meter). This average particle diameter is smaller than the average particle diameter 1.0  $\mu m$  of  $Y_2O_3$  before mixing.

The raw slurry of the resulting thermistor material was granulated and dried to obtain a granulated powder of the thermistor material. The grinding conditions of the pearl mill device and drying conditions of the spray drier are the same as those of Example 7. The molding is performed by the molding method in the same manner as in Example 7 to obtain a thermistor element, which is incorporated into a typical temperature sensor assay to give a temperature sensor.

The evaluation results are shown in Table 8. Regarding the temperature sensor of Example 11, a temperature accuracy of  $\pm 30^\circ C$  can be obtained. The evaluation method of the temperature accuracy is the same as that of Example 7.

In Example 11, the thermistor element incorporated into the temperature sensor shows temperature characteristics with good resistivity as the object of the present invention. That is, it shows low resistivity (50 to 100 k $\Omega$ ), good resistivity temperature coefficient  $\beta$  (2000 to 4000 (K)) and small change in resistivity ( $\pm 10\%$  or less).

(Example 12)

In Example 12, a ball mill as a conventional method is used in the grinding step (mixing and grinding) in the second preparation step in Example 8. As the raw material for obtaining a mixed sintered body of  $Y(CrMn)O_3$  and  $Y_2O_3$ ,  $(Mn_{1.5}Cr_{1.5})O_4$  and  $Y_2O_3$  are used. In the first preparation step,  $(Mn_{1.5}Cr_{1.5})O_4$  is obtained in the same manner as in the first preparation step of Example 8.

In the second preparation step, for the purpose of obtaining the desired resistivity and resistivity temperature coefficient,  $(Mn_{1.5}Cr_{1.5})O_4$  (average particle diameter: 2 to 5  $\mu m$ , 158 g) and  $Y_2O_3$  (average particle diameter: 1.0  $\mu m$ , 342 g) are first weighed to make 500 g as the total amount. In addition,  $SiO_2$  and  $CaCO_3$  are used as a sintering auxiliary, and  $SiO_2$  (15 g) and  $CaCO_3$  (23 g) are added (compounding 2). Accordingly, 538 g of the total of  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$ ,  $SiO_2$  and  $CaCO_3$  is used as the mixing/grinding raw material.

Regarding the operation conditions of the mixing and grinding, the mixing and grinding are performed in the same manner as in Example 11. The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was 2.7  $\mu m$ . This average particle diameter is smaller than the average particle diameter (1.0  $\mu m$ ) of  $Y_2O_3$  before mixing.

The raw slurry of the resulting thermistor material is granulated and dried to obtain a granulated powder of the thermistor material. The grinding conditions of the pearl mill device and drying conditions of the spray drier



are the same as those of Example 7. The molding is performed by the molding method in the same manner as in Example 7 to obtain a thermistor element, which is incorporated into a typical temperature sensor assay to give a temperature sensor.

The evaluation results are shown in Table 8. Regarding the temperature sensor of Example 12, a temperature accuracy of  $\pm 30^{\circ}\text{C}$  can be obtained. The evaluation method of the temperature accuracy is the same as that of Example 7. Also in Example 11, the thermistor element incorporated into the temperature sensor shows temperature characteristics with good resistivity.

(Example 13)

In Example 13, a ball mill as a conventional method is used in the grinding step (mixing and grinding) in the second preparation step of Example 9. As the raw material for obtaining a mixed sintered body of  $\text{Y}(\text{CrMn})\text{O}_3$  and  $\text{Y}_2\text{O}_3$ ,  $\text{Y}(\text{CrMn})\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{TiO}_2$  are used. In the first preparation step,  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$  is obtained in the same manner as in the first preparation step of Example 7.

In the second preparation step, for the purpose of obtaining the desired resistivity and resistivity temperature coefficient,  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$  (average particle diameter: 2 to 5  $\mu\text{m}$ , 380 g),  $\text{Y}_2\text{O}_3$  (average particle diameter: 1.0  $\mu\text{m}$ , 100 g) and  $\text{TiO}_3$  (20 g) are first weighed to make 500 g as the total amount. In addition,  $\text{SiO}_2$  and  $\text{CaCO}_3$  are used as a sintering auxiliary, and  $\text{SiO}_2$  (15 g) and  $\text{CaCO}_3$  (23 g) are added (compounding 2). Accordingly, 538 g of the total of  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{CaCO}_3$  is used as the mixing/grinding raw material.

Regarding the operation conditions of the mixing and grinding, the mixing and grinding are performed in the same manner as in Example 11. The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was 3.0  $\mu\text{m}$  (micron

meter). This average particle diameter is smaller than the average particle diameter  $1.0\mu\text{ m}$  of  $\text{Y}_2\text{O}_3$  before mixing.

5 The raw slurry of the resulting thermistor material is granulated and dried to obtain a granulated powder of the thermistor material. The grinding conditions of the pearl mill device and drying conditions of the spray drier are the same as those of Example 7. The molding is performed by the molding method in the same manner as in 10 Example 7 to obtain a thermistor element, which is incorporated into a typical temperature sensor assay to give a temperature sensor.

The evaluation results are shown in Table 8. Regarding the temperature sensor of Example 13, a 15 temperature accuracy of  $\pm 25^\circ\text{C}$  can be obtained. The evaluation method of the temperature accuracy is the same as that of Example 13.

Also in Example 12, the thermistor element incorporated into the temperature sensor shows temperature 20 characteristics with good resistivity.

(Example 14)

In Example 14, a ball mill as a conventional method is used in the grinding step (mixing and grinding) in the second preparation step of Example 10. As the raw 25 material for obtaining a mixed sintered body of  $\text{Y}(\text{CrMnTi})\text{O}_3$  and  $\text{Y}_2\text{O}_3$ ,  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$ ,  $\text{Y}_2\text{O}_3$  and  $\text{TiO}_2$  are used. In the first preparation step,  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  is obtained in the same manner as in the first preparation step of Example 8.

In the second preparation step, for the purpose of 30 obtaining the desired resistivity and resistivity temperature coefficient,  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  (average particle diameter: 2 to 5  $\mu\text{ m}$ , 145 g),  $\text{Y}_2\text{O}_3$  (average particle diameter: 1.0  $\mu\text{ m}$ , 338 g) and  $\text{TiO}_2$  (17 g) are first weighed to make 500 g as the total amount. In addition, 35  $\text{SiO}_2$  and  $\text{CaCO}_3$  are used as a sintering auxiliary, and  $\text{SiO}_2$  (15 g) and  $\text{CaCO}_3$  (23 g) are added (compounding 2). Accordingly, 538 g of the total of  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$ ,  $\text{Y}_2\text{O}_3$ ,

TiO<sub>2</sub>, SiO<sub>2</sub> and CaCO<sub>3</sub> is used as the mixing/grinding raw material.

Regarding the operation conditions of the mixing and grinding, the mixing and grinding are performed in the same manner as in Example 11. The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was 3.0  $\mu$  m. This average particle diameter is smaller than the average particle diameter (1.0  $\mu$  m) of Y<sub>2</sub>O<sub>3</sub> before mixing.

The raw slurry of the resulting thermistor material is granulated and dried to obtain a granulated powder of the thermistor material. The grinding conditions of the pearl mill device and drying conditions of the spray drier are the same as those of Example 7. The molding is performed by the molding method in the same manner as in Example 7 to obtain a thermistor element, which is incorporated into a typical temperature sensor assay to give a temperature sensor.

The evaluation results are shown in Table 8. Regarding the temperature sensor of Example 14, a temperature accuracy of  $\pm 25^{\circ}\text{C}$  can be obtained. The evaluation method of the temperature accuracy is the same as that of Example 7.

Also in Example 14, the thermistor element incorporated into the temperature sensor shows temperature characteristics with good resistivity as in Example 11.

As described above, when Examples 7 to 14 are compared, all thermistor elements show temperature characteristics with good resistivity as the object of the present invention, but it can be said that the production methods described in Examples 7 to 10 are superior in temperature accuracy of a sensor to those described in Examples 11 to 14.

That is, in the production methods described in Examples 7 to 10, uniform mixing of the composition is realized by atomization of the thermistor material while

accomplishing the effect described in the above first aspect and a variation in composition of a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  is reduced, thereby making it possible to reduce scatter in resistivity.

5           Accordingly, in case that the thermistor element of the present invention is produced by the production method according to the second embodiment (Examples 7 to 10), it is possible to provide a thermistor element capable of improving the temperature accuracy at room temperature to 1000°C to  $\pm 10^\circ\text{C}$  or less in comparison with the production process using a conventional ball mill (Examples 1 to 14, temperature accuracy:  $\pm 20$  to  $30^\circ\text{C}$ ) and realizing high accuracy of the temperature sensor.

(Example 15)

15           In Example 15, a mixed sintered body ( $M^1 = Y$ ,  $M^2 = Cr, Mn$ ) of  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$  is obtained from  $Y_2O_3$ ,  $Cr_2O_3$ ,  $Mn_2O_3$  and  $CaCO_3$  as the raw material. A flow chart illustrating a production step of the thermistor element of Example 15 is shown in Fig. 15.

20           This Example relates to the first production method described in the above third embodiment. That is, the above precursor is obtained in the first preparation step (from compounding 1 to  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$ ), and a medium stirring mill is used in the grinding step of the mixing step of the first preparation step and the grinding step of the second preparation step (starting from compounding 2 in the figure).

25            $Y_2O_3$ ,  $Cr_2O_3$ ,  $Mn_2O_3$  and  $CaCO_3$  (the purity of all components is not less than 99.9%) are prepared. In the compounding 1, these components are compounded so that the desired resistivity and resistivity temperature coefficient as the thermistor element can be obtained.

30           Specifically,  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  are weighed so that a and b (molar fraction) (a:b) of  $aY(Cr_{0.5}Mn_{0.5})O_3 \cdot bY_2O_3$  becomes 38:62 to make 2000 g as the total amount. Furthermore, 36 g of  $CaCO_3$  is added and 2036 g of the total of  $Y_2O_3$ ,  $Cr_2O_3$ ,  $Mn_2O_3$  is used as a mixed raw material.

In the following mixing step, a medium stirring mill is used to atomize the raw material. As the medium stirring mill, a pearl mill device (manufactured by Ashizawa Co., Ltd., RV1V, effective volume: 1.0 liter, actual volume: 0.5 liter) is used. Regarding the mixing conditions of this pearl mill device, 3.0 kg of zirconia balls having a diameter of 0.5 mm are used as a grinding medium and 80% of the volume of a stirring vessel are filled with zirconia balls.

The operation conditions are as follows:  
circumferential rate: 12 m/sec, revolution: 3110 rpm.  
Using 4.5 liter of distilled water as a dispersing medium relative to 2036 g of the mixed raw material, a dispersant and a binder are added, followed by mixing and grinding for 10 hours. As the binder, polyvinyl alcohol (PVA) is added in an amount of 20 g per 2036 g of the mixed raw material.

The raw slurry of the thermistor material subjected to the mixing/grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was 0.4  $\mu$  m (micron meter). This average particle diameter is smaller than the average particle diameter (1.0  $\mu$  m) of  $Y_2O_3$  and smaller than 0.5  $\mu$  m.

The raw slurry of the resulting thermistor material is dried under the conditions of a drying chamber inlet temperature of 200°C and an outlet temperature of 120°C by using a spray drier. The resulting granulated powders of the thermistor material are spherical powders having an average particle diameter of 30  $\mu$  m, and this raw material powder is charged in a crucible made of 99.3%  $Al_2O_3$  and then calcined in a high-temperature oven in the air at 1100 to 1300°C for 1 to 2 hours to obtain a precursor  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$  (calcination step).

The precursor  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$  as a bulk solid obtained in the calcination was roughly ground by using a



have the same structure as that of thermistor elements and temperature sensors shown in Fig. 2 to Fig. 4.

Then, the temperature sensor was put in a high-temperature furnace and resistivity temperature characteristics are evaluated within the range from room temperature (e.g. 27°C, etc.) to 1000°C in the same manner as in Example 1. The evaluation results are shown in Table 9. The temperature accuracy of the resulting temperature sensor are evaluated in the same manner as in Example 7. The results are shown in Table 10.

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Table &lt;Example 9&gt;

No.	Raw material composition (mol %)		Resistivity (k $\Omega$ )		Resistivity temperature coefficient (K)	Change in resistivity (%)
	Y (Cr <sub>0.5</sub> Mn <sub>0.5</sub> )O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Room temperature (27°C)	1000°C		
19	38	62	50	0.14	2450	-5.0
20	95	5	30	0.10	2240	-4.0
21	5	95	100	0.20	2440	-4.0



Table &lt;Example 10&gt;

	Raw material component in case of grinding	Average particle diameter after grinding ( $\mu$ m)	Average particle diameter after grinding ( $\mu$ m)	Temperature accuracy ( $^{\circ}$ C)
Example 15	$Y(CrMn)O_3 \cdot Y_2O_3$	0.4	0.4	$\pm 7$
Example 16	$Y(CrMn)O_3$ and $Y_2O_3$	0.3	0.4	$\pm 5$
Example 17	$Y(CrMn)O_3 \cdot Y_2O_3$	0.4	1.8	$\pm 10$
Example 18	$Y(CrMn)O_3$ and $Y_2O_3$	0.3	1.8	$\pm 10$
Example 19	$Y(CrMn)O_3 \cdot Y_2O_3$	2.0	3.0	$\pm 30$
Example 20	$Y(CrMn)O_3$ and $Y_2O_3$	1.7	2.7	$\pm 25$
Comparative Example 1	$Y(Cr_{0.5}Mn_{0.5})O_3$	2.0	3.0	$\pm 30$
Comparative Example 2	$YTiO_3$	2.0	3.0	$\pm 25$
Comparative Example 3				

In Table 10, the raw material component in case of grinding represents a raw material component in the grinding step of the second preparation step ( $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3 \cdot \text{Y}_2\text{O}_3$  in this Example), the average particle diameter ( $\mu\text{m}$ ) after mixing represents an average particle diameter of a raw slurry after grinding in the mixing step of the first preparation step ( $0.4\ \mu\text{m}$  in this Example) and the average particle diameter ( $\mu\text{m}$ ) after grinding represents an average particle diameter of a raw slurry after grinding in the grinding step of the second preparation step ( $0.3\ \mu\text{m}$  in this Example). The same rule applies correspondingly to the following Examples 16 to 20 and Comparative Examples 1 and 2 evaluated in Comparative Example 3.

Regarding the temperature sensor of Example 15, a temperature accuracy of  $\pm 7^\circ\text{C}$  can be obtained.

Furthermore, in the compounding 1, a thermistor element was produced by using a thermistor raw material prepared so that a molar ratio (a:b) of  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3:\text{Y}_2\text{O}_3$  becomes 95:5 and 5:95 in the same manner as described above and the thermistor element was evaluated. The results (resistivity temperature characteristics) are shown in Table 9. In Example 15, the respective elements are referred to as an element No. 19, an element No. 20 and an element No. 21 in the sequence of the above molar ratio a:b, e.g. 38:62, 95:5 and 5:95. They are shown in Table 9.

As shown in Table 9, the thermistor element of Example 15 shows low resistivity of 50 to  $100\ \text{k}\Omega$  required of a temperature sensor within the range where the molar fraction ( $a + b = 1$ ) of  $a\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3 \cdot b\text{Y}_2\text{O}_3$  satisfy the relations:  $0.05 \leq a < 1$  and  $0 < b \leq 0.95$ , and also shows a resistivity temperature coefficient  $\beta$  of 2000 to 4000 (K), and is capable of widely controlling the resistivity and resistivity temperature coefficient. Therefore, it is possible to detect a temperature ranging from room temperature to high temperature of  $1000^\circ\text{C}$ .

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The resulting raw slurry is granulated and dried by using a spray drier in the same manner as in Example 15, and then calcined to obtain  $Y(Cr_{0.5}Mn_{0.5})O_3$ .  $Y(Cr_{0.5}Mn_{0.5})O_3$  as a bulk solid obtained in the temporary calcination is roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a powder of  $Y(Cr_{0.5}Mn_{0.5})O_3$ .

In the following compounding 2, compounding is performed so that the desired resistivity and resistivity temperature coefficient as the thermistor element can be obtained. Specifically,  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$  are weighed so that a to b (a:b) of  $aY(Cr_{0.5}Mn_{0.5})O_3 \cdot bY_2O_3$  becomes 38:62 to make 2000 g as the total amount.

In the grinding step,  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$  are mixed and ground by using a pearl mill device similar to the mixing step to perform atomization. The grinding conditions of the pearl mill device are the same as those of the mixing step. In this grinding step, a dispersant, a binder and a releasent are added, followed by mixing and further steps.

The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was  $0.4 \mu m$  (micron meter). This average particle diameter is smaller than the average particle diameter  $1.0 \mu m$  of  $Y_2O_3$  before compounding in the compounding 2.

The slurry of  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$  obtained after grinding is granulated, molded and then calcined to obtain a thermistor element in the same manner as in Example 15. This thermistor element is incorporated into a temperature sensor assay to give a temperature sensor in the same manner as in Example 15.

The resulting thermistor element and temperature sensor have the same structure as that of thermistor elements and temperature sensors shown in Fig. 2 to Fig. 4.

The above temperature sensor was evaluated in the same manner as in Example 15. The evaluation results of the resistivity temperature characteristics are shown in Table 11 and those of the temperature accuracy are shown in Table 10.

Table <Example 11>

No.	Raw material composition (mol %)		Resistivity (k $\Omega$ )		Resistivity temperature coefficient (K)	Change in resistivity (%)
	Y(Cr <sub>0.5</sub> Mn <sub>0.5</sub> )O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Room temperature (27°C)	1000°C		
22	38	62	60	0.15	2350	-7.0
23	95	5	40	0.11	2300	-5.0
24	5	95	100	0.22	2400	-5.0

Regarding the temperature sensor of Example 16, a temperature accuracy of  $\pm 5^{\circ}\text{C}$  can be obtained, as shown in Table 10. In Example 16, grinding and atomization are performed by using a medium stirring mill in the mixing  
10 step of the first preparation step and grinding step of the second preparation step. Therefore, there can be provided a thermistor element whose temperature accuracy is improved in comparison with Example 7 (temperature accuracy:  $\pm 10^{\circ}\text{C}$ ) wherein grinding and atomization were  
15 performed only in the latter step using a medium stirring mill.

Furthermore, a thermistor element was produced by using a thermistor raw material prepared so that a molar ratio (a:b)  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3:\text{Y}_2\text{O}_3$  becomes 95:5 and 5:95 in the  
20 grinding step in the same manner as described above and the thermistor element was evaluated. The results are shown in Table 11. In Example 16, the respective elements are referred to as an element No. 22, an element No. 23 and an element No. 24 in the sequence of the above molar  
25 ratio a:b, e.g. 38:62, 95:5 and 5:95. They are shown in Table 11.

As shown in Table 11, the thermistor element of Example 16 shows the low resistivity of 50 to 100  $\text{k}\Omega$  required of a temperature sensor within the range where  
30 the molar fraction ( $a + b = 1$ ) of  $a\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3 \cdot b\text{Y}_2\text{O}_3$  satisfy the relations:  $0.05 \leq a < 1$  and  $0 < b \leq 0.95$ , and also shows a resistivity temperature coefficient  $\beta$  of 2000 to 4000 (K), and is capable of widely controlling the resistivity and resistivity temperature coefficient.  
35 Therefore, it is possible to detect a temperature ranging from room temperature to high temperature of  $1000^{\circ}\text{C}$ .

As is apparent from the results of the high-

temperature durability test (change in resistivity), a wide-range type thermistor material having stable characteristics (e.g. small change in resistivity), etc.) can be provided.

5 (Example 17)

In Example 17, a mixed sintered body ( $M^1 = Y$ ,  $M^2 = Cr, Mn$ ) of  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$  is obtained from  $Y_2O_3$ ,  $Cr_2O_3$ ,  $Mn_2O_3$  and  $CaCO_3$  as the raw material. A flow chart illustrating a production step of the thermistor element of Example 17 is shown in Fig. 17.

Example 17 relates to the first production method described in the above third embodiment. That is, the above precursor is obtained in the first preparation step (from compounding 1 to  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$ ), a medium stirring mill is used in the grinding step of the mixing step of the first preparation step and a ball mill is used in the grinding step of the second preparation step (starting from compounding 2 in the figure). That is, the ball mill is used in place of the medium stirring mill in the grinding step in Example 15.

The first preparation step of this Example is the same as that of Example 15 and its description is omitted. Also in Example 17, a and b (molar fraction) (a:b) of  $aY(Cr_{0.5}Mn_{0.5})O_3 \cdot bY_2O_3$  is 38:62. The raw slurry of the thermistor material subjected to the mixing/grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was  $0.4 \mu m$  (micron meter).

In the following compounding 2, a powder (2000 g) of the precursor  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$  obtained in the first preparation step is prepared.

In the following grinding step, a ball mill device is used to add a dispersant, a binder and a releasant to  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$  prepared in the compounding 2, followed by mixing and further grinding.

Regarding the grinding conditions of this ball mill device, the powder (2000 g) prepared in the compounding 2



is charged in a resin pot (volume: 20 liter) containing  $\text{Al}_2\text{O}_3$  pebbles having a diameter of 15  $\phi$  (10 kg) and pebbles having a diameter of 20  $\phi$  (10 kg) and, after adding 6000 cc of purified water, the mixture was mixed and ground at 60 rpm for 6 hours.

The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was 1.8  $\mu\text{m}$ . This average particle diameter is smaller than the average particle diameter (1.0  $\mu\text{m}$ ) of  $\text{Y}_2\text{O}_3$  before compounding in the compounding 1.

The slurry of  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$  and  $\text{Y}_2\text{O}_3$  obtained after grinding was granulated, molded and then calcined to obtain a thermistor element in the same manner as in Example 15. This thermistor element is incorporated into a temperature sensor assay to give a temperature sensor in the same manner as in Example 15. The resulting thermistor element and temperature sensor have the same structure as that of thermistor elements and temperature sensors shown in Fig. 2 to Fig. 4.

Then, the above temperature sensor was evaluated in the same manner as in Example 15. The resistivity temperature characteristics were the same as those of Example 15 (resistivity temperature characteristics of a:b = 38:62 in Fig. 24). In addition, the evaluation results of the temperature accuracy are shown in Table 10. Regarding the temperature sensor of Example 17, a temperature accuracy of  $\pm 10^\circ\text{C}$  can be obtained as in Example 17.

Furthermore, a thermistor element was produced by using a thermistor raw material prepared so that a molar ratio of  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3:\text{Y}_2\text{O}_3$  becomes 95:5 and 5:95 in the mixing step and the thermistor element was evaluated. As a result, the resistivity temperature characteristics of this thermistor element were good and the same as those of the thermistor element having the same molar ratio as that of Example 15 (see Table 9).

Accordingly, the thermistor element of Example 17 shows low resistivity of 50 to 100 k $\Omega$  required as a temperature sensor within the range where the molar fraction ( $a + b = 1$ ) of  $aY(Cr_{0.5}Mn_{0.5})O_3 \cdot bY_2O_3$  satisfy the relations:  $0.05 \leq a < 1$  and  $0 < b \leq 0.95$ , and also shows a resistivity temperature coefficient  $\beta$  of 2000 to 4000 (K), and is capable of widely controlling the resistivity and resistivity temperature coefficient. Therefore, it is possible to detect a temperature ranging from room temperature to high temperature of 1000°C.

As is apparent from the results of the high-temperature durability test (change in resistivity), a wide-range type thermistor material having stable characteristics (e.g. small change in resistivity), etc.) can be provided.

(Example 18)

In Example 18, a mixed sintered body ( $M^1 = Y$ ,  $M^2 = Cr, Mn$ ) of  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$  is obtained from  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$ . A flow chart illustrating a production step of the thermistor element of Example 18 is shown in Fig. 18.

Example 18 relates to the second production method described in the above third embodiment. That is,  $Y(Cr_{0.5}Mn_{0.5})O_3$  is obtained in the first preparation step (from compounding 1 to  $Y(Cr_{0.5}Mn_{0.5})O_3$ ), a medium stirring mill is used in the mixing step of the first preparation step and a ball mill is used in the grinding step of the second preparation step (starting from compounding 2 in the figure). That is, the ball mill is used in place of the medium stirring mill in the grinding step in Example 16.

The first preparation step of this Example is the same as that of Example 6 and its description is omitted. Also in Example 18, the raw slurry of the thermistor material subjected to the mixing/grinding treatment in the mixing step in the compounding 1 was evaluated by using a laser type granulometer. As a result, the average

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particle diameter was  $0.3 \mu\text{m}$  (micrometer).

Then, a powder of temporarily calcined  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$  is obtained from the first preparation step.

In the following compounding 2, for the purpose of obtaining the desired resistivity and resistance temperature coefficient as the thermistor element,  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$  (powder) and  $\text{Y}_2\text{O}_3$  are weighed so that a and b (a:b) of  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$  (powder) and  $b\text{Y}_2\text{O}_3$  becomes 38:62, to make 2000 g as the total amount.

In the following grinding step, a ball mill device is used to mix and grind  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$  and  $\text{Y}_2\text{O}_3$  weighed in the compounding 2. Regarding the grinding conditions of this ball mill device, the mixed weighed substance (2000 g) is charged in a resin pot (volume: 20 liter) containing  $\text{Al}_2\text{O}_3$  pebbles having a diameter of  $15 \phi$  (10 kg) and pebbles having a diameter of  $20 \phi$  (10 kg) and, after adding 6000 cc of purified water, the mixture was mixed and ground at 60 rpm for 6 hours.

The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was  $1.8 \mu\text{m}$ . This average particle diameter is smaller than the average particle diameter ( $1.0 \mu\text{m}$ ) of  $\text{Y}_2\text{O}_3$  before compounding in the compounding 2. In the mixing and grinding step, a dispersant, a binder and a releasant are added and, at the same time, the mixture is ground.

The slurry of  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3 \cdot \text{Y}_2\text{O}_3$  obtained after grinding was granulated, molded and then calcined to obtain a thermistor element in the same manner as in Example 15. This thermistor element is incorporated into a temperature sensor assay to give a temperature sensor in the same manner as in Example 15. The resulting thermistor element and temperature sensor have the same structure as that of thermistor elements and temperature sensors shown in Fig. 2 to Fig. 4.

Then, the above temperature sensor was evaluated in

the same manner as in Example 15. The resistivity temperature characteristics were the same as those of Example 16 (resistivity temperature characteristics of a:b = 38:62 in Fig. 11).

5           In addition, the evaluation results of the temperature accuracy are shown in Table 10. Regarding the temperature sensor of Example 18, a temperature accuracy of  $\pm 10^{\circ}\text{C}$  can be obtained as in Example 17.

10           Furthermore, a thermistor element was produced by using a thermistor raw material prepared so that a molar ratio of  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3:\text{Y}_2\text{O}_3$  becomes 95:5 and 5:95 in the mixing step and the thermistor element was evaluated. As a result, the resistivity temperature characteristics of this thermistor element were good and the same as those  
15           (see Table 11) of the thermistor element having the same molar ratio as that of Example 16.

          Accordingly, the thermistor element of Example 18 shows low resistivity of 50 to 100  $\text{k}\Omega$  required as a temperature sensor within the range where the molar  
20           fraction ( $a + b = 1$ ) of  $a\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3 \cdot b\text{Y}_2\text{O}_3$  satisfy the relations:  $0.05 \leq a < 1$  and  $0 < b \leq 0.95$ , and also shows a resistivity temperature coefficient  $\beta$  of 2000 to 4000 (K), and is capable of widely controlling the resistivity and resistivity temperature coefficient. Therefore, it is  
25           possible to detect a temperature ranging from room temperature to high temperature of  $1000^{\circ}\text{C}$ .

          As is apparent from the results of the high-temperature durability test (change in resistivity), a wide-range type thermistor material having stable  
30           characteristics (e.g. small change in resistivity), etc.) can be provided.

(Example 19)

          Example 19 is basically the same as Example 15 and Example 17. That is, a precursor is formed by using  $\text{Y}_2\text{O}_3$ ,  
35            $\text{Cr}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{CaCO}_3$  as the raw material to obtain a mixed sintered body ( $\text{M}^1 = \text{Y}$ ,  $\text{M}^2 = \text{Cr}$ ,  $\text{Mn}$ ) of  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3 \cdot \text{Y}_2\text{O}_3$ . A flow chart illustrating a production step of the

thermistor element of Example 19 is shown in Fig. 19.

In Example 19, a ball mill device as a conventional method is used in the mixing step and grinding step in the production method of Example 15.

5 In the same manner as in Example 15,  $Y_2O_3$ ,  $Cr_2O_3$ ,  $Mn_2O_3$  and  $CaCO_3$  (all of the purity is not less than 99.9%) are prepared. In the compounding 1, these respective components are compounded to obtain the desired resistivity and resistivity temperature coefficient as the  
10 thermistor element.

Specifically,  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  are weighed so that a and b (molar fraction) (a:b) of  $aY(Cr_{0.5}Mn_{0.5})O_3 \cdot bY_2O_3$  becomes 38:62 to make 2000 g as the total amount. Furthermore, 36 g of  $CaCO_3$  is added and 2036 g of the total  
15 of  $Y_2O_3$ ,  $Cr_2O_3$ ,  $Mn_2O_3$  and  $CaCO_3$  is used as a mixed raw material.

Then, this mixed raw material is mixed and ground by using a ball mill device in the mixing step. Regarding the operation conditions, the thermistor raw material is  
20 charged in a resin pot (volume: 20 liter) containing  $Al_2O_3$  pebbles having a diameter of 15  $\phi$  (10 kg) and pebbles having a diameter of 20  $\phi$  (10 kg) and, after adding 6000 cc of purified water, the mixture was mixed and ground at 60 rpm for 6 hours.

25 The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was 2.0  $\mu$  m. This average particle diameter is smaller than the average particle diameter (1.0  $\mu$  m) of  
30  $Y_2O_3$  before mixing.

The raw slurry of the resulting thermistor material is dried under the conditions of a drying chamber inlet temperature of 200°C and an outlet temperature of 120°C by using a spray drier. The resulting granulated powders of  
35 the thermistor material are spherical powders having an average particle diameter of 30  $\mu$  m, and this raw material powder is charged in a crucible made of 99.3%  $Al_2O_3$  and

The precursor  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$  as a bulk solid  
5 obtained in the calcination was roughly ground by using a  
chaser mill and passed through a sieve (# 30 mesh) to  
obtain a powder of precursor  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$ .

The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser type granulometer. As a result, the average particle diameter was 3.0  $\mu$  m (micron meter).

Then, the temperature sensor was evaluated in the same manner as in Example 15. The resistivity temperature characteristics of this thermistor element were good and the same as those of the thermistor element having the same molar ratio (a:b = 38:62) as that of Example 15 (see Table 9).

(Example 20)

Example 20 is basically the same as Example 16 and Example 18. That is,  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$  is formed by using  $\text{Y}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{CaCO}_3$  as the raw material in the

temporary calcination to obtain a mixed sintered body ( $M^1 = Y$ ,  $M^2 = Cr, Mn$ ) of  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$ . A flow chart illustrating a production step of the thermistor element of Example 20 is shown in Fig. 20.

5 In Example 20, a ball mill device as a conventional method is used in the mixing step and grinding step in the production method of Example 16.

In the same manner as in Example 16,  $Y_2O_3$ ,  $Cr_2O_3$ ,  $Mn_2O_3$  and  $CaCO_3$  (all of the purity is not less than 99.9%)  
10 are prepared. In the compounding 1,  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  are weighed so that a molar ratio of  $Y:Cr:Mn$  becomes 2:1:1 to make 644 g as the total amount. Furthermore, 36 g of  $CaCO_3$  is added and 680 g of the total of  $Y_2O_3$ ,  $Cr_2O_3$ ,  $Mn_2O_3$  and  $CaCO_3$  is used as a mixed raw material.

15 In the mixing step, the mixed raw material obtained in the compounding 1 is mixed and ground by using a ball mill device. Regarding the operation conditions, the thermistor raw material is charged in a resin pot (volume: 5 liter) containing  $Al_2O_3$  pebbles having a diameter of 15  
20 mm $\phi$  (2.5 kg) and pebbles having a diameter of 20 mm $\phi$  (2.5 kg) and, after adding 1800 cc of purified water, the mixture was mixed and ground at 60 rpm for 6 hours.

The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser  
25 type granulometer. As a result, the average particle diameter was 1.7  $\mu m$ . This average particle diameter is smaller than the average particle diameter (1.0  $\mu m$ ) of  $Y_2O_3$  before mixing.

The raw slurry of the resulting thermistor material  
30 is granulated, dried and then temporarily calcined to obtain  $Y(Cr_{0.5}Mn_{0.5})O_3$  in the same manner as in Example 15.  $Y(Cr_{0.5}Mn_{0.5})O_3$  as a bulk solid obtained in the temporary calcination was roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a powder of  
35  $Y(Cr_{0.5}Mn_{0.5})O_3$ .

In the following compounding 2, for the purpose of obtaining desired resistivity and resistivity temperature

coefficient,  $Y(Cr_{0.5}Mn_{0.5})O_3$  and  $Y_2O_3$  are first weighed so that a and b (molar fraction) (a:b) of  $aY(Cr_{0.5}Mn_{0.5})O_3 \cdot bY_2O_3$  becomes 38:62, to make 2000 g as the total amount.

A ball mill device is used to atomize  
5  $Y(Cr_{0.5}Mn_{0.5})O_3 \cdot Y_2O_3$  in the grinding step similar to in mixing step. Regarding the grinding conditions of this ball mill device, the thermistor raw material obtained in the compounding 2 is charged in a resin pot (volume: 20 liter) containing  $Al_2O_3$  pebbles having a diameter of 15  $\phi$   
10 (10 kg) and pebbles having a diameter of 20  $\phi$  (10 kg) and, after adding 6000 cc of purified water, the mixture was mixed and ground at 60 rpm for 6 hours.

The raw slurry of the thermistor material subjected to the grinding treatment was evaluated by using a laser  
15 type granulometer. As a result, the average particle diameter was 2.7  $\mu m$  (micron meter).

The resulting raw slurry of the thermistor material is granulated, dried, molded and then fired to obtain a thermistor element in the same manner as in Example 15.  
20 This thermistor element is incorporated into a temperature sensor assay to give a temperature sensor in the same manner as in Example 15. The resulting thermistor element and temperature sensor have the same structure as that of thermistor elements and temperature sensors shown in Fig.  
25 2 to Fig. 4.

Then, the above temperature sensor was evaluated in the same manner as in Example 15. The resistivity temperature characteristics were the same as those of Example 16 having the same molar ratio (a:b = 38:62) (see  
30 Table 11).

In addition, the evaluation results of the temperature accuracy are shown in Table 10. The temperature accuracy of the temperature sensor of Example 20 is  $\pm 25^\circ C$ .

35 (Comparative Example 3)

In Comparative Examples 1 and 2, the average particle diameter ( $\mu m$ ) after mixing, average particle

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diameter ( $\mu$  m) after grinding and temperature were evaluated in the same manner as in Example 15. The results are shown in Table 10.

As described above, when Examples 15 to 20 are compared, all thermistor elements show temperature characteristics with good resistivity as the object of the present invention.

Regarding the temperature sensor, however, the production methods of Examples 15 to 18 according to the production method of the above third embodiment are superior to those of Examples 19 and 20. Furthermore, the production methods of Examples 15 and 16 are superior to those of Examples 17 and 18.

That is, the larger the number of steps of performing atomization using the medium stirring mill so that the particle diameter of the raw material is smaller than a predetermined value in the mixing step in the first preparation step before firing and grinding step in the second preparation step, the more the temperature accuracy is improved.

#### (Other Modification Examples)

By the way, it is also possible to provide a wide-range type thermistor element comprising a mixed sintered body of  $Y(CrMnTi)O_3$  and  $Y_2O_3$  as in Examples 3 to 6 from a composition of  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $(Mn_{1.5}Cr_{1.5})O_4$  and  $TiO_2$  or from  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $(Mn_{1.5}Cr_{1.5})O_4$ ,  $Y_2O_3$  and  $YTiO_3$ , other than Examples 1 to 20.

It is possible to prepare a wide-range type thermistor element composed of a mixed sintered body of  $Y(CrMn)O_3$  and  $Y_2O_3$  like Examples 1 and 2 from a yttrium compound (e.g.  $Y_2O_3$ , etc.), a chromium compound (e.g.  $Cr_2O_3$ , etc.) and a manganese compound (e.g.  $Mn_2O_3$ , etc.), as a matter of course.

It is also possible to prepare a wide-range type thermistor element composed of a mixed sintered body of  $Y(CrMnTi)O_3$  and  $Y_2O_3$  like Examples 3 to 6 from a yttrium compound (e.g.  $Y_2O_3$ , etc.), a chromium compound (e.g.

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calcination, thereby making it possible to obtain a thermistor element.

It is also possible to form a thermistor element by forming a lead wire after calcining the cylindrical molded article.

It is also possible to obtain a thermistor element provided with a lead wire by adding a binder, a resin material, etc. to raw materials of the thermistor element, mixing them, adjusting the viscosity and hardness of the mixture to those suitable for extrusion molding, performing extrusion molding of the mixture to obtain a molded article of the thermistor element with a hole for providing a lead wire, inserting the lead wire, followed by calcination.

It is also possible to obtain a thermistor element provided with a lead wire by adding a binder, a resin material, etc. to raw materials of the thermistor element, mixing them, adjusting the viscosity and hardness of the mixture to those suitable for sheet molding, performing sheet molding of the mixture to obtain a sheet-like thermistor sheet having a thickness of  $200 \mu m$ , laminating five thermistor sheets each other to form a laminate having a thickness of 1 mm, molding the laminate in a mold to obtain a molded article of a thermistor element with a hole having a diameter of  $0.4 mm\phi$  for providing a lead wire having an outer diameter of  $1.8 mm\phi$ , inserting the lead wire, followed by firing.

The present invention was described hereinabove, but the thermistor element of the present invention is a material represented by the general formula:  
 $aM^1M^2O_3 \cdot b(Y_2O_3)$ , composed of a mixed sintered body of  $M^1M^2O_3$  showing low resistivity and low resistance temperature coefficient (e.g. 1000 to 4000 (K)) and  $Y_2O_3$  as a material for stabilizing the resistivity of the thermistor element.

Consequently, since the resistivity and resistance temperature coefficient can be widely controlled by appropriately mixing both components and calcining the

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mixture, it is possible to provide a thermistor element which can detect a temperature ranging from room temperature to high temperature of 1000°C and has stable characteristics (e.g. no change in resistivity, etc.) in view of the reliability of heat history from room temperature to 1000°C (Examples 1 to 20).

According to the method of producing the thermistor element of the present invention, uniform mixing of the composition is realized by atomization of the thermistor raw material and scatter in resistivity of the thermistor element is reduced by reducing a variation in composition, thereby making it possible to provide a thermistor element wherein the temperature accuracy is improved to  $\pm 10^\circ\text{C}$  or less at room temperature to 1000°C ( $\pm 25$  to  $30^\circ\text{C}$  in the prior art) and high accuracy of the temperature sensor can be realized (Examples 7 - 10 and 15 - 18).

(Example 21)

In this Example,  $\text{Y}(\text{CrMnTi})\text{O}_3$ , wherein Y was selected as  $\text{M}^1$ , Cr and Mn were selected as  $\text{M}^2$  and Ti was selected as  $\text{M}^3$  in  $\text{M}^1(\text{M}^2\text{M}^3)\text{O}_3$ , is obtained.

A flow chart illustrating a production step of the thermistor element of Example 21 is shown in Fig. 21.

First,  $\text{Y}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{TiO}_2$  (purity of all components is not less than 99.9%) are prepared and then weighed so that a molar ratio of Y:Cr:Mn:Ti becomes 100:48:48:4 to make 500 g as the total amount in the step of the compounding 1 (compounding 1). Then, the total amount of these weighed substances is charged in a resin pot (volume: 5 liter) containing  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  pebbles having a diameter of 15  $\phi$  (2.5 kg) and pebbles having a diameter of 20  $\phi$  (2.5 kg) and, after adding 1500 cc of purified water, the mixture was mixed at 60 rpm for 6 to 12 hours.

A mixed slurry of  $\text{Y}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{TiO}_2$  obtained after a mixing treatment is transferred to a porcelain evaporating dish, and then dried by using a hot-air dryer

at 150°C for 12 hours or more to obtain a mixed solid of  $Y_2O_3$ ,  $Cr_2O_3$ ,  $Mn_2O_3$  and  $TiO_2$ .

Subsequently, this mixed solid is roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a mixed powder of  $Y_2O_3$ ,  $Cr_2O_3$ ,  $Mn_2O_3$  and  $TiO_2$ .

This mixed powder is charged in a crucible made of 99.3%  $Al_2O_3$  and then calcined in a high-temperature oven in the air at 1100 to 1300°C for 1 to 2 hours to obtain  $Y(Cr_{0.48}Mn_{0.48}Ti_{0.04})O_3$ .  $Y(Cr_{0.48}Mn_{0.48}Ti_{0.04})O_3$  as a bulk solid obtained in the calcination was roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a powder.

In the step of the compounding 2,  $SiO_2$  and  $CaCO_3$ , which are converted into a liquid phase within the range from 1500 to 1650°C, are used as a sintering auxiliary in case of firing and  $SiO_2$  and  $CaCO_3$  are added in an amount of 3% by weight and 4.5% by weight, respectively, based on the total amount of the above  $Y(Cr_{0.48}Mn_{0.48}Ti_{0.04})O_3$ .

In the mixing and grinding step, the above  $Y(Cr_{0.48}Mn_{0.48}Ti_{0.04})O_3$ ,  $Y_2O_3$ ,  $SiO_2$  and  $CaCO_3$  are charged in a resin pot (volume: 5 liter) containing  $Al_2O_3$  or  $ZrO_2$  pebbles having a diameter of 15  $\phi$  (2.5 kg) and pebbles having a diameter of 20  $\phi$  (2.5 kg), in order to mix these weighed substances. After adding 1500 cc of purified water, the mixture was mixed at 60 rpm for 4 or more hours and then ground. In this case, polyvinyl alcohol (PVA) as a binder is added in an amount of 1 g per 100 g of a  $Y(Cr_{0.48}Mn_{0.48}Ti_{0.04})O_3$  powder while mixing, followed by grinding.

A mixed ground slurry of  $Y(Cr_{0.48}Mn_{0.48}Ti_{0.04})O_3$  obtained after mixing and grinding is granulated and dried by using a spray dryer to obtain a granulated powder of  $Y(Cr_{0.48}Mn_{0.48}Ti_{0.04})O_3$ . This granulated powder is used as a thermistor raw material.

Subsequently, using this thermistor raw material and a lead wire (material:  $Pt_{100}$  (pure platinum)) having a size of 0.3 mm $\phi$  in outer diameter x 10.5 mm in length, the

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lead wire is inserted and the thermistor raw material is molded in a mold having an outer diameter of 1.74 mm $\phi$  under a pressure of about 1000 kgf/cm<sup>2</sup> to obtain a molded article of a thermistor element (provided with a lead  
5 wire) having an outer diameter of 1.75 mm $\phi$  .

The molded article of the thermistor element is arranged on a corrugated setter made of Al<sub>2</sub>O<sub>3</sub> and then calcined in the air at 1400 to 1600°C for 1 to 2 hours to obtain a thermistor element having an outer diameter of  
10 1.60 mm $\phi$  .

This thermistor element 1 has a structure as shown in Fig. 3, and is composed of lead wires 11, 12 and an element portion 13 (prepared by calcining a molded article of the above thermistor element). The thermistor element  
15 1 is incorporated into a typical temperature sensor as shown in Fig. 4 and Fig. 5 to give a temperature sensor. Thus, a temperature sensor using a thermistor having a composition of element No. 23 in Table 12 is obtained.

As shown in Fig. 5, a metal pipe 3 is filled with a magnesia powder 33 to secure insulating properties of lead  
20 wires 11, 12, 31, 32 in the metal pipe 3.

The temperature sensor was put in a high-temperature oven and temperature characteristics of the resistivity were evaluated within the range from room temperature  
25 (27°C) to 1000°C.

Using the temperature sensor, with respect to a change in resistivity of the temperature sensor in a high-temperature durability test in the air at 1100°C for 100 hours, a resistivity after 100 hours to an initial  
30 resistivity was evaluated by the following change in resistivity  $\Delta R$ .

$$\Delta R (\%) = (\text{Resistivity after 100 hours} / \text{Initial resistivity}) \times 100 - 100$$

Furthermore, in the step of the compounding 1, thermistor element materials were prepared according to  
35 the compositions of elements No. 31, No. 32, No. 34 and No. 34 by changing the molar ratio of Y:Cr:Mn:Ti, as shown

in Table 12, and thermistor elements were made and the resulting temperature sensors were evaluated. The respective resistance characteristics of the compositions of the elements No. 31 to No. 35 are shown in Table 12.

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Table <Example 12>

No.	Composition of thermistor element (mol %)	Resistivity (kΩ )		Resistivity temperature coefficient (K)	Change in resistivity (%)
		Room temperature (27°C)	1000°C		
31	Y(Cr <sub>0.495</sub> Mn <sub>0.495</sub> Ti <sub>0.01</sub> )O <sub>3</sub>	60	0.1	2510	-5.0
32	Y(Cr <sub>0.49</sub> Mn <sub>0.49</sub> Ti <sub>0.02</sub> )O <sub>3</sub>	80	0.1	2620	-4.0
33	Y(Cr <sub>0.48</sub> Mn <sub>0.48</sub> Ti <sub>0.04</sub> )O <sub>3</sub>	100	0.1	2710	-4.0
34	Y(Cr <sub>0.47</sub> Mn <sub>0.47</sub> Ti <sub>0.06</sub> )O <sub>3</sub>	200	0.08	3070	-4.0
35	Y(Cr <sub>0.455</sub> Mn <sub>0.455</sub> Ti <sub>0.09</sub> )O <sub>3</sub>	300	0.06	3340	-4.0



5           As shown in this table, the wide-range type  
thermistor material of this Example shows the resistivity  
of 50 to 100 k $\Omega$  required as a temperature sensor.  
Therefore, it is possible to detect a temperature ranging  
from room temperature to high temperature of 1000°C.

10           The resistivity temperature coefficient  $\beta$  was  
calculated by the resistivity at room temperature (27°C)  
and that at 1000°C.

          As is apparent from the results of the high-  
temperature durability test, it can be confirmed that a  
15 wide-range type thermistor material having stable  
characteristics (e.g. small change in resistivity), etc.)  
is provided.

(Example 22)

          In this Example,  $M^1(M^2M^3)O_3$  wherein Y was selected as  
20  $M^1$ , Cr and Mn were selected as  $M^2$  and Ti was selected as  
 $M^3$ , i.e.,  $Y(CrMnTi)O_3$ , is obtained, and is prepared from  
(MnCr) $O_4$  spinel,  $Y_2O_3$  and  $TiO_2$ .

          A flow chart illustrating a production step of the  
thermistor element of Example 22 is shown in Fig. 22.

25           (MnCr) $O_4$  spinel is prepared as follows. That is,  
 $Cr_2O_3$  and  $Mn_2O_3$  (purity of all components is not less than  
99.9%) are first prepared and then weighed so that a molar  
ratio Cr:Mn becomes 1:1 to make 500 g as the total amount  
(compounding 1). Then, the total amount of these weighed  
30 substances is charged in a resin pot (volume: 5 liter)  
containing  $Al_2O_3$  or  $ZrO_2$  pebbles having a diameter of 15  $\phi$   
(2.5 kg) and pebbles having a diameter of 20  $\phi$  (2.5 kg)  
and, after adding 1500 cc of purified water, the mixture  
was mixed at 60 rpm for 6 to 12 hours. A mixed slurry of  
35  $Cr_2O_3$  and  $Mn_2O_3$  obtained after a mixing treatment is  
transferred to a porcelain evaporating dish, and then

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dried by using a hot-air dryer at 150°C for 12 hours or more to obtain a mixed solid of  $\text{Cr}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$ .

Subsequently, this mixed solid is roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a mixed powder of  $\text{Cr}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$ . This mixed powder is charged in a crucible made of 99.3%  $\text{Al}_2\text{O}_3$  and then temporarily calcined in a high-temperature oven in an atmosphere under a normal pressure (in the air) at 1100 to 1300°C for 1 to 2 hours to obtain  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$ .  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  as a bulk solid obtained in the temporary calcination was roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a powder.

In the following step of the compounding 2, for the purpose of obtaining the composition of the element No. 33 in Table 12,  $(\text{MnCr})\text{O}_4$  spinel,  $\text{Y}_2\text{O}_3$  and  $\text{TiO}_2$  are weighed to make 500 g as the total amount, followed by mixing and grinding treatment. In the same manner as in Example 21,  $\text{SiO}_2$  and  $\text{CaCO}_3$  are added as a sintering auxiliary, but  $\text{SiO}_2$  and  $\text{CaCO}_3$  are added in an amount of 3% by weight and 4.5% by weight, respectively, based on the total amount of the above  $(\text{Mn}_{1.5}\text{Cr}_{1.5})\text{O}_4$  and  $\text{Y}_2\text{O}_3$ .

The above  $(\text{MnCr})\text{O}_4$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{CaCO}_3$  are charged in a resin pot (volume: 5 liter) containing  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  pebbles having a diameter of 15 mmφ (2.5 kg) and pebbles having a diameter of 20 mmφ (2.5 kg). After adding 500 cc of purified water, the mixture was mixed at 60 rpm for 4 or more hours and then ground.

Mixing, grinding, granulation, molding and firing are performed in the same manner as in Example 21 to obtain a thermistor element. This thermistor and a temperature sensor made by incorporating this thermistor element have the same structure as that shown in Fig. 3 to Fig. 5 like Example 21. The temperature sensor is evaluated in the same manner as in Example 21.

Furthermore, in the step of the compounding 2, thermistor element were prepared by adjusting a molar ratio of  $(\text{MnCr})\text{O}_4$  spinel,  $\text{Y}_2\text{O}_3$  and  $\text{TiO}_2$  becomes the

compositions of elements No. 31, No. 32, No. 34 and No. 35 in Table 12, and thermistor elements were made and the resulting temperature sensors were evaluated.

As a result, according to the production method of Example 22, the same results as in Table 12 are obtained. Therefore, the wide-range type thermistor element of this Example can provide a wide-range type thermistor element having stable characteristics causing little change in resistivity.

(Example 23)

In this Example,  $M^1(M^2M^3)O_3$  wherein Y was selected as  $M^1$ , Cr and Mn were selected as  $M^2$  and Ti was selected as  $M^3$ , i.e.,  $Y(CrMnTi)O_3$ , is obtained, and  $Y(CrMnTi)O_3$  is prepared from  $Y(CrMn)O_3$ ,  $Y_2O_3$  and  $TiO_2$ .

A flow chart illustrating a production step of the thermistor element of Example 23 is shown in Fig. 23.

In the production of  $Y(CrMn)O_3$ ,  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  (purity of all components is not less than 99.9%) are first prepared and then weighed so that a molar ratio Y:Cr:Mn becomes 2:1:1 to make 500 g as the total amount (compounding 1).

Then, the total amount of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  is charged in a resin pot (volume: 5 liter) containing  $Al_2O_3$  or  $ZrO_2$  pebbles having a diameter of 15 mm $\phi$  (2.5 kg) and pebbles having a diameter of 20 mm $\phi$  (2.5 kg) and, after adding 1500 cc of purified water, the mixture was mixed at 60 rpm for 6 to 12 hours. A mixed slurry of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  obtained after a mixing treatment is transferred to a porcelain evaporating dish, and then dried by using a hot-air dryer at 150°C for 12 hours or more to obtain a mixed solid of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$ .

Subsequently, the mixed solid of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  is roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a mixed powder of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$ . The mixed powder of  $Y_2O_3$ ,  $Cr_2O_3$  and  $Mn_2O_3$  is charged in a crucible made of 99.3%  $Al_2O_3$  and then calcined in a high-temperature oven in the air at 1100 to

1300°C for 1 to 2 hours to obtain  $Y(Cr_{0.5}Mn_{0.5})O_3$ .

$Y(Cr_{0.5}Mn_{0.5})O_3$  as a bulk solid obtained in the calcination was roughly ground by using a chaser mill and passed through a sieve (# 30 mesh) to obtain a powder.

5           In the step of the compounding 2, for the purpose of obtaining the composition of the element No. 33 in Table 12,  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $TiO_2$  are weighed to make 500 g as the total amount, followed by mixing and grinding treatment. In the same manner as in Examples 21 to 22,  
10        $SiO_2$  and  $CaCO_3$  are added as a sintering auxiliary, but  $SiO_2$  and  $CaCO_3$  are added in an amount of 3% by weight and 4.5% by weight, respectively, based on the total amount of the above  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $TiO_2$ .

          In the mixing and grinding step, the above  
15        $Y(CrMn)O_3$ ,  $Y_2O_3$ ,  $TiO_2$ ,  $SiO_2$  and  $CaCO_3$  are charged in a resin pot (volume: 5 liter) containing  $Al_2O_3$  or  $ZrO_2$  pebbles having a diameter of 15  $\phi$  (2.5 kg) and pebbles having a diameter of 20  $\phi$  (2.5 kg). After adding 1500 cc of purified water, the mixture was mixed at 60 rpm for 4 or  
20       more hours and then ground.

          Mixing, grinding, granulation, molding and firing are performed in the same manner as in Example 21 to obtain a thermistor element. This thermistor and a temperature sensor made by incorporating this thermistor  
25       element have the same structure as that, shown in Fig. 3 to Fig. 5, of Example 21. The temperature sensor is evaluated in the same manner as in Example 21.

          Furthermore, in the step of the compounding 2, thermistor element were prepared by adjusting a molar  
30       ratio of  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $TiO_2$  becomes the compositions of elements No. 31, No. 32, No. 34 and No. 35 in Table 12, and thermistor elements were made and the resulting temperature sensors were evaluated.

          As a result, according to the production method of  
35       Example 23, the same results as in Table 12 are obtained. Therefore, the wide-range type thermistor element of this Example can provide a wide-range type thermistor element

having stable characteristics causing little change in resistivity.

(Example 24)

In this Example,  $M^1(M^2M^3)O_3$  wherein Y was selected as  
5  $M^1$ , Cr and Mn were selected as  $M^2$  and Ti was selected as  
 $M^3$ , i.e.,  $Y(CrMnTi)O_3$ , is obtained, and  $Y(CrMnTi)O_3$  is  
prepared from  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $YTiO_3$ .

A flow chart illustrating a production step of the  
thermistor element of Example 24 is shown in Fig. 24.  
10  $Y(CrMn)O_3$  is prepared in the same process as in Example 23  
(Compounding 2).

In the compounding 2 step,  $YTiO_3$  is prepared as  
follows. That is,  $Y_2O_3$  and  $TiO_2$  (purity of all components  
is not less than 99.9%) are first prepared and then weighed  
15 so that a molar ratio of Y:Ti becomes 1:1 to make 500 g as  
the total amount. Then, the total amount of the weighed  
substances is charged in a resin pot (volume: 5 liter)  
containing  $Al_2O_3$  or  $ZrO_2$  pebbles having a diameter of 15  $\phi$   
(2.5 kg) and pebbles having a diameter of 20  $\phi$  (2.5 kg)  
20 and, after adding 1500 cc of purified water, the mixture  
was mixed at 60 rpm for 6 hour. A mixed slurry of  $Y_2O_3$  and  
 $TiO_2$  obtained after a mixing treatment is transferred to a  
porcelain evaporating dish, and then dried by using a hot-  
air dryer at 150°C for 12 hours or more to obtain a mixed  
25 solid of  $Y_2O_3$  and  $TiO_2$ .

Subsequently, the mixed solid of  $Y_2O_3$  and  $TiO_2$  is  
roughly ground by using a chaser mill and passed through a  
sieve (# 30 mesh) to obtain a mixed powder of  $Y_2O_3$  and  
 $TiO_2$ . The mixed powder is charged in a crucible made of  
30 99.3%  $Al_2O_3$  and then calcined in a high-temperature oven in  
the air at 1100 to 1300°C for 1 to 2 hours to obtain  $YTiO_3$ .  
 $YTiO_3$  as a bulk solid obtained in the calcination was  
roughly ground by using a chaser mill and passed through a  
sieve (# 30 mesh) to obtain a powder.

35 In the step of the compounding 3, for the purpose of  
obtaining the composition of the element No. 3 in Table  
12,  $Y(Cr_{0.5}Mn_{0.5})O_3$ ,  $Y_2O_3$  and  $YTiO_3$  are weighed to make 500 g

as the total amount, followed by mixing and grinding treatment. In the same manner as in Examples 21 to 22,  $\text{SiO}_2$  and  $\text{CaCO}_3$  are added as a sintering auxiliary, but  $\text{SiO}_2$  and  $\text{CaCO}_3$  are added in an amount of 3% by weight and 4.5% by weight, respectively, based on the total amount of the above  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{YTiO}_3$ .

The above  $\text{Y}(\text{CrMn})\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{YTiO}_3$ ,  $\text{SiO}_2$  and  $\text{CaCO}_3$  are charged in a resin pot (volume: 5 liter) containing  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  pebbles having a diameter of 15  $\phi$  (2.5 kg) and pebbles having a diameter of 20  $\phi$  (2.5 kg). After adding 1500 cc of purified water, the mixture was mixed at 60 rpm for 4 or more hours and then ground.

Mixing, grinding, granulation, molding and firing are performed in the same manner as in Example 21 to obtain a thermistor element. This thermistor and a temperature sensor made by incorporating this thermistor element have the same structure as that shown in Table 12 like Example 21. The temperature sensor is evaluated in the same manner as in Example 21.

Furthermore, in the step of the compounding 2, thermistor element were prepared by adjusting a molar ratio of  $\text{Y}(\text{Cr}_{0.5}\text{Mn}_{0.5})\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{YTiO}_3$  becomes the compositions of elements No. 31, No. 32, No. 34 and No. 35 in Table 12, and thermistor elements were made and the resulting temperature sensors were evaluated.

As a result, according to the production method of Example 24, the same results as in Table 12 are obtained. Therefore, the wide-range type thermistor element of this Example can provide a wide-range type thermistor element having stable characteristics causing little change in resistivity.

(Example 25)

In this Example,  $\text{Y}(\text{CrMnTi})\text{O}_3$ , wherein Y was selected as  $\text{M}^1$ , Cr and Mn were selected as  $\text{M}^2$  and Ti was selected as  $\text{M}^3$  in  $\text{M}^1(\text{M}^2\text{M}^3)\text{O}_3$ , is obtained, and  $\text{Y}(\text{CrMnTi})\text{O}_3$  is prepared from  $(\text{MnCr})\text{O}_4$  spinel,  $\text{Y}_2\text{O}_3$  and  $\text{YTiO}_3$ .

A flow chart illustrating a production step of the thermistor element of Example 25 is shown in Fig. 25. (MnCr)O<sub>4</sub> spinel is prepared in the manner similar to in Example 22. YTiO<sub>3</sub> is prepared in the manner similar to in Example 24.

In the step of the compounding 3, for the purpose of obtaining the composition of the element No. 33 in Table 12, (MnCr)O<sub>4</sub> spinel, Y<sub>2</sub>O<sub>3</sub> and YTiO<sub>3</sub> are weighed to make 500 g as the total amount, followed by mixing and grinding treatment. In the same manner as in the above respective Examples, SiO<sub>2</sub> and CaCO<sub>3</sub> are used as a sintering auxiliary and SiO<sub>2</sub> and CaCO<sub>3</sub> are added in an amount of 3% by weight and 4.5% by weight, respectively, based on the total amount of the above (MnCr)O<sub>4</sub> spinel, Y<sub>2</sub>O<sub>3</sub> and YTiO<sub>3</sub>.

Then, the above (MnCr)O<sub>4</sub> spinel, Y<sub>2</sub>O<sub>3</sub>, YTiO<sub>3</sub> are charged in a resin pot (volume: 5 liter) containing Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub> pebbles having a diameter of 15 mmφ (2.5 kg) and pebbles having a diameter of 20 mmφ (2.5 kg) and, after adding 1500 cc of purified water, the mixture was mixed at 60 rpm for 4 or more hours.

Mixing, grinding, granulation, molding and firing are performed in the same manner as in Example 21 to obtain a thermistor element.

The thermistor element has a structure as shown in Table 12, and is incorporated into a typical temperature sensor assay to give a temperature sensor. The temperature sensor is evaluated in the same manner as in Example 21.

Furthermore, in the step of the compounding 2, thermistor element were prepared by adjusting a molar ratio of (MnCr)O<sub>4</sub> spinel, Y<sub>2</sub>O<sub>3</sub> and YTiO<sub>3</sub> becomes the compositions of elements No. 31, No. 32, No. 34 and No. 35 in Table 10, and thermistor elements were made and the resulting temperature sensors were evaluated.

As a result, according to the production method of Example 25, the same results as in Table 12 are obtained. Therefore, the wide-range type thermistor element of this Example can provide a wide-range type thermistor element

having stable characteristics causing little change in resistivity.

As described in Examples 21 to 25, when  $Y(CrMnTi)O_3$  is represented as  $Y((CrMn)_aTi_b)O_3$ , a molar fraction of the total of Cr and Mn is a, a molar fraction of Ti is b and a + b = 1, if  $0 < b < 0.1$ , the resistivity is stable in view of heat history from room temperature to 1000°C. Therefore, it is possible to realize a wide-range type thermistor element having the resistivity of 60 to 300 kΩ within the temperature range from room temperature to 1000°C.

Accordingly, it is possible to provide a wide-range type thermistor element which can detect a temperature ranging from room temperature to high temperature of 1000°C and has stable characteristics (e.g. no change in resistivity, etc.) in view of the reliability of heat history from room temperature to 1000°C.

By the way, it is also possible to provide a wide-range type thermistor element having the composition of  $Y(CrMnTi)O_3$  from the composition of  $Y(CrMn)O_3$ ,  $(MnCr)O_4$  spinel,  $Y_2O_3$  and  $TiO_2$  or the composition of  $Y(CrMn)O_3$ ,  $(MnCr)O_4$  spinel,  $Y_2O_3$  and  $YTiO_3$ , other than Examples 21 to 25.

It is possible to prepare a wide-range type thermistor material having the composition of  $Y(CrMnTi)O_3$ , like Examples 21 to 25, from an yttrium compound (e.g.  $Y_2O_3$ , etc.), a chromium compound (e.g.  $Cr_2O_3$ , etc.) and a titanium compound (e.g.  $TiO_2$ , etc.), as a matter of course.

In Examples 21 to 26, the mixed solid is hot-air dried before firing, roughly ground by using a chaser mill and then calcined. It is also possible to provide the above wide-range type thermistor element by adding a binder in the mixing step, granulating and drying a mixed powder and calcining the mixed powder in order to realize the uniformity of the composition.

To realize uniformity of the composition, a wide-range type thermistor element can also be provided by



In Examples 21 to 25, as the lead wire, a wire (material: Pt<sub>100</sub> (pure platinum)) having a wire diameter of 0.3 mmφ and a length of 10.5 mm was used, but the shape, wire diameter and length of the lead wire can be optionally selected according to the shape, dimension and service atmosphere/condition of the temperature sensor. The material of the lead wire is not limited to Pt<sub>100</sub> (pure platinum), and there can also be used a high-melting temperature metal having a melting point enough to endure the calcination temperature of the thermistor element and providing satisfactory conductivity as the lead wire, e.g. Pt<sub>80</sub>Ir<sub>20</sub> (platinum 80%, iridium 20%), etc.

In Examples 21 to 25, as a molding method of the thermistor element, molding is performed after inserting the lead wire. It is also possible to form a lead wire by molding a thermistor raw material (powder) to form a cylindrical molded article, making a hole for providing the lead wire, inserting the lead wire, followed by calcination, thereby making it possible to obtain a thermistor element.

It is also possible to obtain a thermistor element provided with a lead wire by adding a binder, a resin material, etc. to raw materials of the thermistor element, mixing them, adjusting the viscosity and hardness of the mixture to those suitable for sheet molding to obtain a sheet-like thermistor sheet having a thickness of 200  $\mu$  m.

laminating five thermistor sheets to form a laminate having a thickness of 1 mm, molding the laminate in a mold to obtain a molded article of the thermistor element having an outer diameter of 1.8 mm $\phi$  and a hole, 5 0.4 mm $\phi$  , for providing a lead wire, inserting the lead wire in the hole of the molded article, followed by firing.

It is also possible to obtain a thermistor element provided with a lead wire by adding a binder, a resin 10 material, etc. to raw materials of the thermistor element, mixing them, adjusting the viscosity and hardness of the mixture to those suitable for extrusion molding, performing extrusion molding of the mixture to obtain a molded article of the thermistor element with a hole for 15 providing a lead wire, inserting the lead wire, followed by firing.

(Comparative Example 11)

As Comparative Example 11, Comparative Example of a temperature sensor using a thermistor element having the 20 composition of  $M^1(M^2M^3)O_3$  wherein Y is selected as  $M^1$ , Cr is selected as  $M^2$  and  $M^3$  is not added in  $M^1(M^2M^3)O_3$ , i.e.,  $Y(Cr_{0.5}Mn_{0.5})O_3$ , will be described.

$YCrO_3$  is prepared as follows. That is,  $Y_2O_3$  and  $Cr_2O_3$  (purity of all components is not less than 99.9%) are 25 prepared and then weighed so that a molar ratio of Y:Cr becomes 100:100 in the step of the compounding 1 to obtain  $YCrO_3$  in the same manner as in Example 21. Using the prepared  $YCrO_3$  as the raw material, a temperature sensor is produced and then evaluated. The results are shown in 30 Table 13 (element No. 36). The evaluation was performed in the same manner as in Example 21.



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As is apparent from this table, the resistivity at low temperature range of room temperature (27°C) is remarkably high, e.g. 1000 k $\Omega$  or more. Therefore, the temperature cannot be detected.

As is also apparent from the results of the high-temperature durability test, the change in resistivity  $\Delta R$

exceeds  $\pm 20\%$  and, therefore, a wide-range thermistor element having stable characteristics can not be provided. Accordingly, the thermistor element having the composition of  $YTiO_3$  can not be used as the element of the temperature sensor of the present invention.

(Comparative Example 12)

As Comparative Example 12, Comparative Example of a temperature sensor using a thermistor element having the composition of  $M^1(M^2M^3)O_3$ , wherein Y is selected as  $M^1$ , 50 % by mol of Cr is selected as  $M^2$  and 50% by mol of Mn is selected as  $M^3$  in  $M^1(M^2M^3)O_3$ , i.e.,  $YCrO_3$  will be described.

In the same manner as in Example 21,  $Y(Cr_{0.5}Mn_{0.5})O_3$  is obtained. Using the prepared  $Y(Cr_{0.5}Mn_{0.5})O_3$  as the raw material, a temperature is produced and then evaluated. The results are shown in Table 13 (element No. 37). The evaluation was performed in the same manner as in Example 21.

As is apparent from this table, since the resistivity at high temperature range of  $1000^\circ C$  is too low, the temperature cannot be detected.

As is also apparent from the results of the high-temperature durability test, the change in resistivity  $\Delta R$  exceeds  $\pm 20\%$  and, therefore, a wide-range thermistor element having stable characteristics can not be provided. Accordingly, the thermistor element having the composition of  $Y(CrMn)O_3$  cannot be used as the element of the desired temperature sensor of the present invention.

(Comparative Example 13)

As Comparative Example 13, Comparative Example of a temperature sensor using a thermistor element having the composition of  $YTiO_3$ , wherein Y is selected as  $M^1$ , Ti is selected as  $M^2$  and  $M^3$  is not added in  $M^1(M^2M^3)O_3$ , will be described.

In the same manner as in Example 24,  $YTiO_3$  is obtained. Using the prepared  $YTiO_3$  as the raw material, a temperature is produced and then evaluated. The results

As is apparent from this table, since the thermistor element having the composition of  $\text{YTiO}_3$  shows remarkably high resistivity at low temperature range, i.e. 1000 k $\Omega$  or more, the temperature cannot be detected.

15       The embodiments of the present invention were described hereinabove by way of Examples 21 to 25 and Comparative Examples 11 to 13, but the present invention is of course not limited to these embodiments.

CLAIMS

1. A thermistor element comprising a mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$  of a composition  $M^1M^2O_3$  and  $Y_2O_3$ , wherein  $M^1$  is at least one element selected from the elements of the groups IIA and IIIA excluding La in the Periodic Table, and  $M^2$  is at least one element selected from the elements of the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII.

2. A thermistor element according to claim 1, wherein a and b satisfy the relations  $0.05 \leq a < 1.0$ ,  $0 < b \leq 0.95$  and  $a + b = 1$ , where said a is a molar fraction of  $M^1M^2O_3$  and said b is a molar fraction of  $Y_2O_3$ .

3. A thermistor element according to claim 1 or 2, wherein said  $M^1$  is at least one element selected from Y, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Mg, Ca, Sr, Ba and Sc, and said  $M^2$  is at least one element selected from Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga, Zr, Nb, Mo, Hf, Ta and W.

4. A thermistor element according to claim 3, wherein said  $M^1$  is Y, said  $M^2$  are Cr and Mn, and said mixed sintered body is  $Y(CrMn)O_3 \cdot Y_2O_3$ .

5. A thermistor element according to claim 3, wherein said  $M^1$  is Y, said  $M^2$  are Cr, Mn and Ti, and said mixed sintered body is  $Y(CrMnTi)O_3 \cdot Y_2O_3$ .

6. A thermistor element according to any one of claims 1 to 5, further comprising a sintering auxiliary composed of at least one of  $CaO$ ,  $CaCO_3$  and  $CaSiO_3$ , and  $SiO_2$ .

7. A temperature sensor comprising the thermistor element of claim 1.

8. A method of producing the thermistor element of claim 1, which comprises performing calcination to obtain  $M^1M^2O_3$  having an average particle diameter larger than that of said  $Y_2O_3$ ;

mixing said  $M^1M^2O_3$  with said  $Y_2O_3$ ;  
grinding the mixture to adjust an average particle diameter of the mixture after grinding to an average

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particle diameter which is not more than that of said  $Y_2O_3$  before mixing; molding the mixture into an article having a predetermined shape; and sintering the article.

9. A method of producing the thermistor element of claim 4, which comprises mixing an oxide of Cr with an oxide of Mn; calcining the mixture at  $1000^\circ C$  or more to obtain  $(Mn_{1.5}Cr_{1.5})O_4$  having an average particle diameter larger than that of said  $Y_2O_3$ ;

mixing said  $(Mn_{1.5}Cr_{1.5})O_4$  with said  $Y_2O_3$ ; grinding the mixture to adjust an average particle diameter of the mixture after grinding to an average particle diameter which is not more than that of said  $Y_2O_3$  before mixing; molding the mixture into an article having a predetermined shape; and sintering the article.

10. A method of producing the thermistor element of claim 5, which comprises mixing an oxide of Cr with an oxide of Mn; calcining the mixture at  $1000^\circ C$  or more to obtain  $(Mn_{1.5}Cr_{1.5})O_4$  having an average particle diameter larger than that of said  $Y_2O_3$ ; mixing said  $(Mn_{1.5}Cr_{1.5})O_4$ , said  $Y_2O_3$ , and  $TiO_2$ ; grinding the mixture to adjust an average particle diameter of the mixture after grinding to an average particle diameter which is not more than that of said  $Y_2O_3$  before grinding; molding the mixture into an article having a predetermined shape; and sintering the article.

11. A method of producing a thermistor element of claim 1, which comprises mixing a raw material of said  $M^2$  with a raw material of said  $M^1$ ; grinding the mixture to adjust an average particle diameter of the mixed grind after grinding to an average particle diameter which is not more than that of the raw material of said  $M^1$  before mixing and is not more than  $0.5 \mu m$ ; calcining the mixed grind to obtain said  $M^1M^2O_3$ ;

mixing said  $M^1M^2O_3$  obtained by said calcination with said  $Y_2O_3$ ; molding the mixture into an article having a predetermined shape; and sintering the article.



molding said precursor obtained by said  
calcination into an article having a predetermined shape;  
and sintering the article.

25 mixing said  $M^1M^2O_3$  obtained by said calcination with said  $Y_2O_3$ ; grinding the mixture to adjust an average particle diameter of the mixture after grinding to an average particle diameter which is not more than that of the raw material of said  $Y_2O_3$  before mixing; molding the ground mixture into an article having a predetermined shape; and sintering the article.

14. A method of producing a thermistor element of claim 1, which comprises using those containing at least  $Y_2O_3$  as a raw material of said  $M^1$ ; mixing a raw material of said  $M^2$  with the raw material of said  $M^1$ ; grinding the mixture to adjust an average particle diameter of the mixed grind after grinding to an average particle diameter which is not more than that of the raw material of said  $M^1$  before mixing and is not more than 0.5

$\mu$  m; calcining the ground mixture to obtain a precursor having the same composition as that of said mixed sintered body  $M^1M^2O_3 \cdot Y_2O_3$ ;

grinding said precursor obtained by said  
5 calcination to adjust an average particle diameter of said precursor after grinding to an average particle diameter which is not more than that of the raw material  $Y_2O_3$  as the raw material of said  $M^1$  before mixing; molding the ground precursor into an article having a predetermined shape;  
10 and sintering the article.

15 15. A wide-range type thermistor element comprising a mixed sintered body  $M^1(M^2M^3)O_3$ , wherein  $M^1$  is at least one element selected from the elements of the groups II and IIIA excluding La in the Periodic Table, and  $M^2$  and  $M^3$  respectively represent at least one element selected from the elements of the groups IVA, VA, VIA, VIIA and VIIIA; and wherein

a and b satisfy the relations  $a + b = 1$  and  $0 < b < 0.1$  and, where said a is a molar fraction of  $M^2$  and b is a molar fraction of  $M^3$  in said  $M^1(M^2M^3)O_3$ .  
20

16. A wide-range type thermistor element, wherein said  $M^1$  is at least one element selected from Y, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Mg, Ca, Sr, Ba and Sc, and said  $M^2$  and  $M^3$  respectively represent at least one element  
25 selected from Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga, Zr, Nb, Mo, Zr, Hf, Ta and W.

17. A wide-range type thermistor element according to claim 15 or 16, wherein said  $M^1$  is Y, said  $M^2$  are Cr and Mn, said  $M^3$  is Ti, and said  $M^1(M^2M^3)O_3$  is  $Y(CrMnTi)O_3$ .

30 18. A wide-range type thermistor element according to claim 15, further comprising a sintering auxiliary composed of at least one of  $CaO$ ,  $CaCO_3$  and  $CaSiO_3$ , and  $SiO_2$ .

19. A wide-range type temperature sensor  
35 comprising the thermistor element of claim 15.

20. A wide-range type thermistor element according to claim 16, further comprising a sintering auxiliary

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composed of at least one of  $\text{CaO}$ ,  $\text{CaCO}_3$  and  $\text{CaSiO}_3$ , and  $\text{SiO}_2$ .

21. A wide-range type temperature sensor comprising the thermistor element of claim 16.

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WIDE-RANGE TYPE THERMISTOR ELEMENT AND  
METHOD OF PRODUCING THE SAME

5

ABSTRACT OF THE DISCLOSURE

10           The thermistor element of the present invention is  
composed of a mixed sintered body  $aM^1M^2O_3 \cdot bY_2O_3$  of a  
composition  $M^1M^2O_3$  (wherein  $M^1$  is Y, and  $M^2$  is at least one  
element selected from the elements such as Cr, Mn, Ti,  
etc.) as a perovskite compound and  $Y_2O_3$ , wherein molar  
15       fractions a and b satisfy the relations  $0.05 \leq a < 1.0$ ,  $0$   
 $< b \leq 0.95$  and  $a + b = 1$ . Another wide-range type  
thermistor element of the present invention is composed of  
a perovskite compound  $M^1(M^2M^3)O_3$ , wherein  $M^1$  is at least one  
element selected from the elements of the groups II and  
20       IIIA excluding La in the Periodic Table, and each of  $M^2$  and  
 $M^3$  is at least one element selected from the elements of  
the groups IIB, IIIB, IVA, VA, VIA, VIIA and VIII. a and  
b satisfy the relations  $a + b = 1$  and  $0 < b < 0.1$ , where a  
is a molar fraction of  $M^2$  and b is a molar fraction of  $M^3$   
25       in  $M^1(M^2M^3)O_3$ .

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Fig. 1

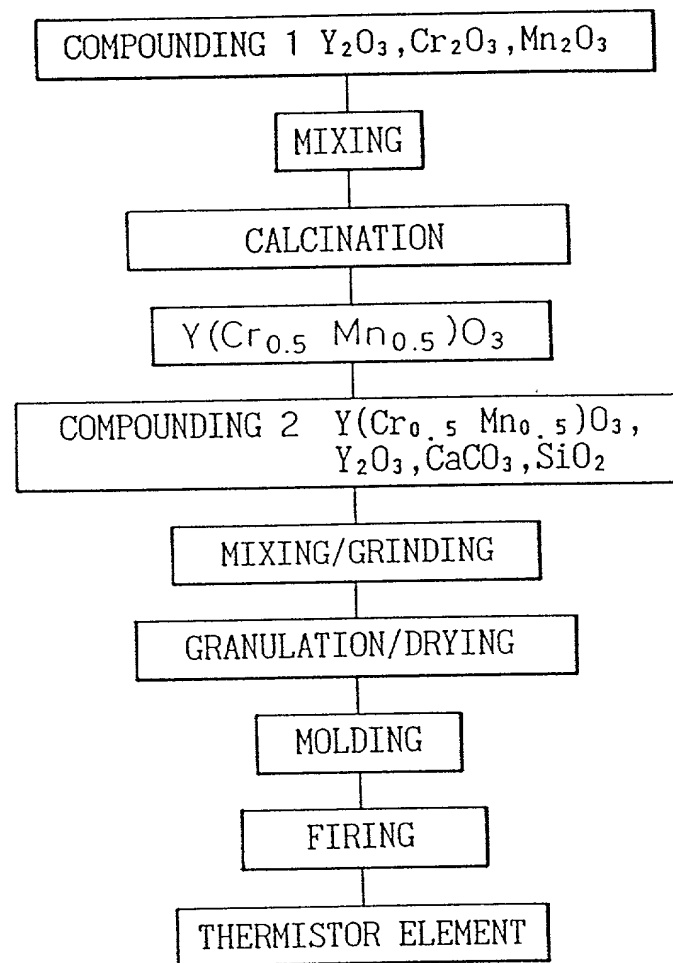


Fig. 2

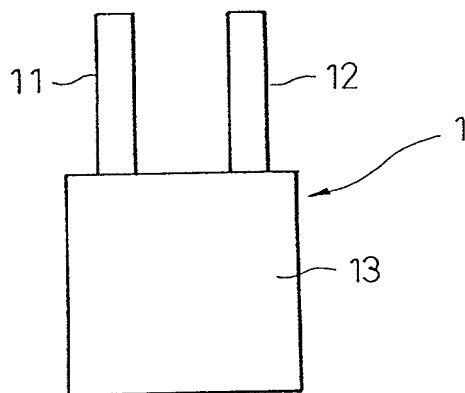


Fig. 3

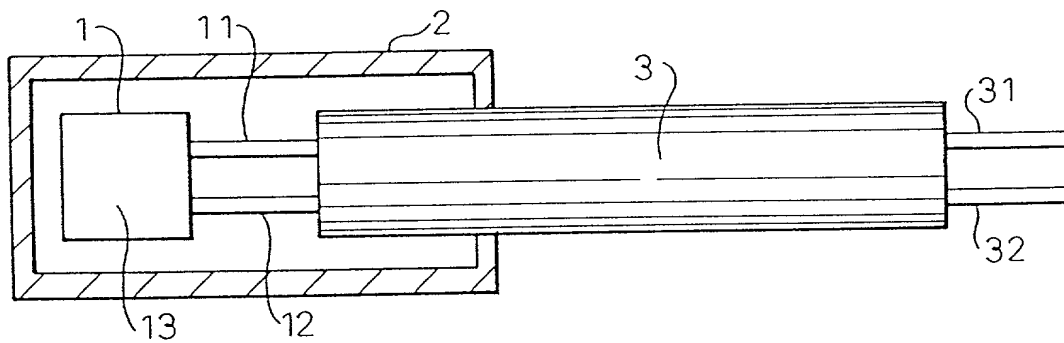


Fig. 4

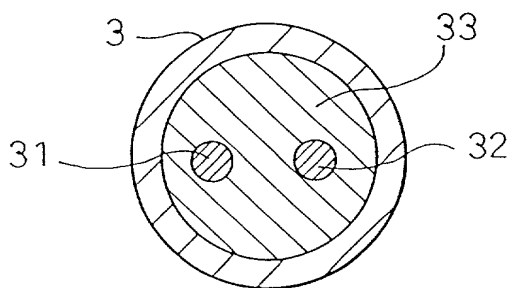


Fig. 5

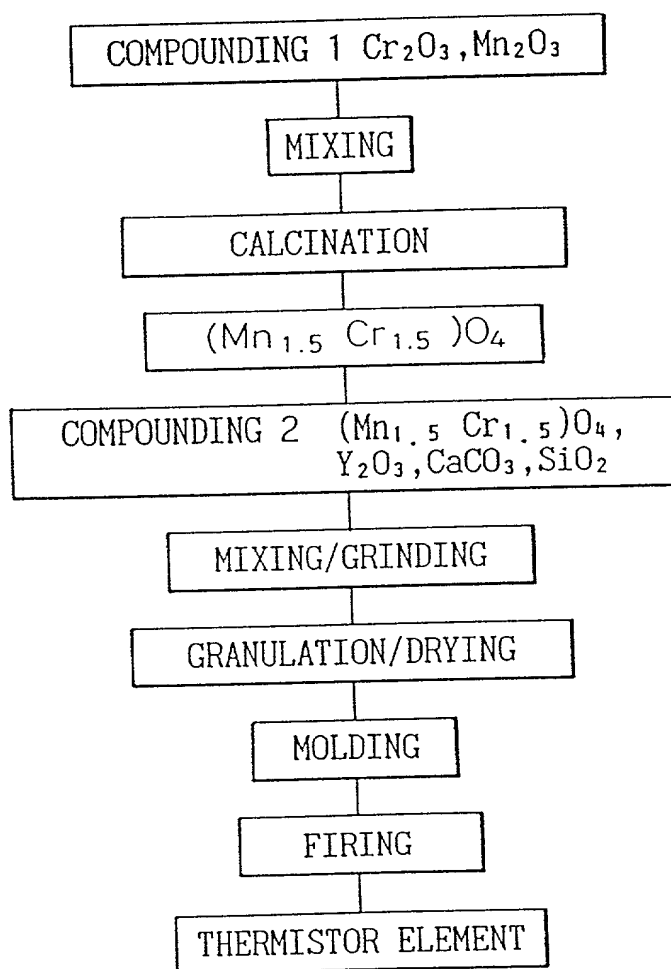


Fig. 6

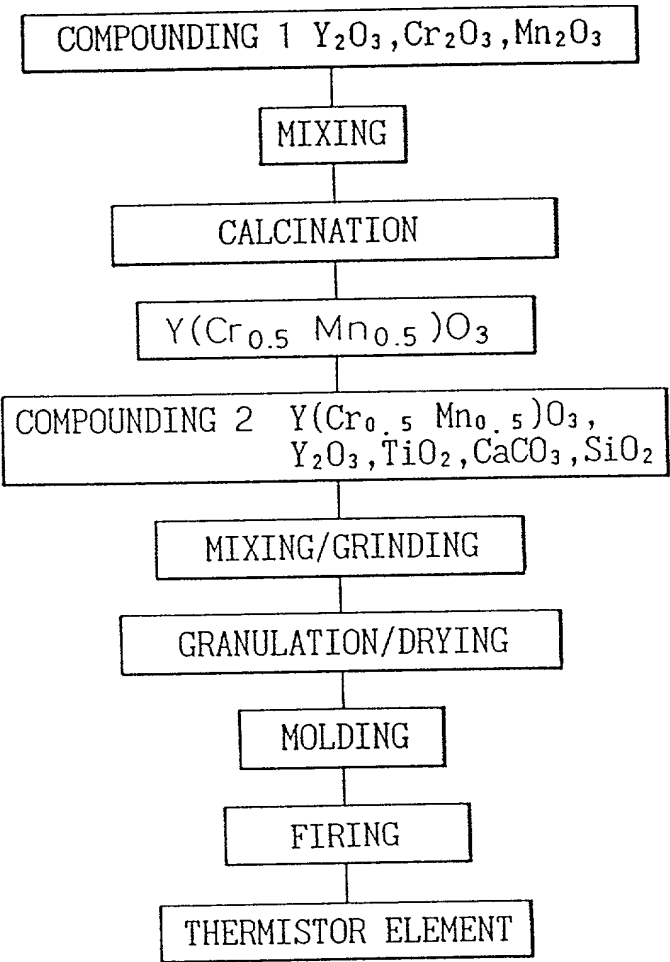




Fig. 7

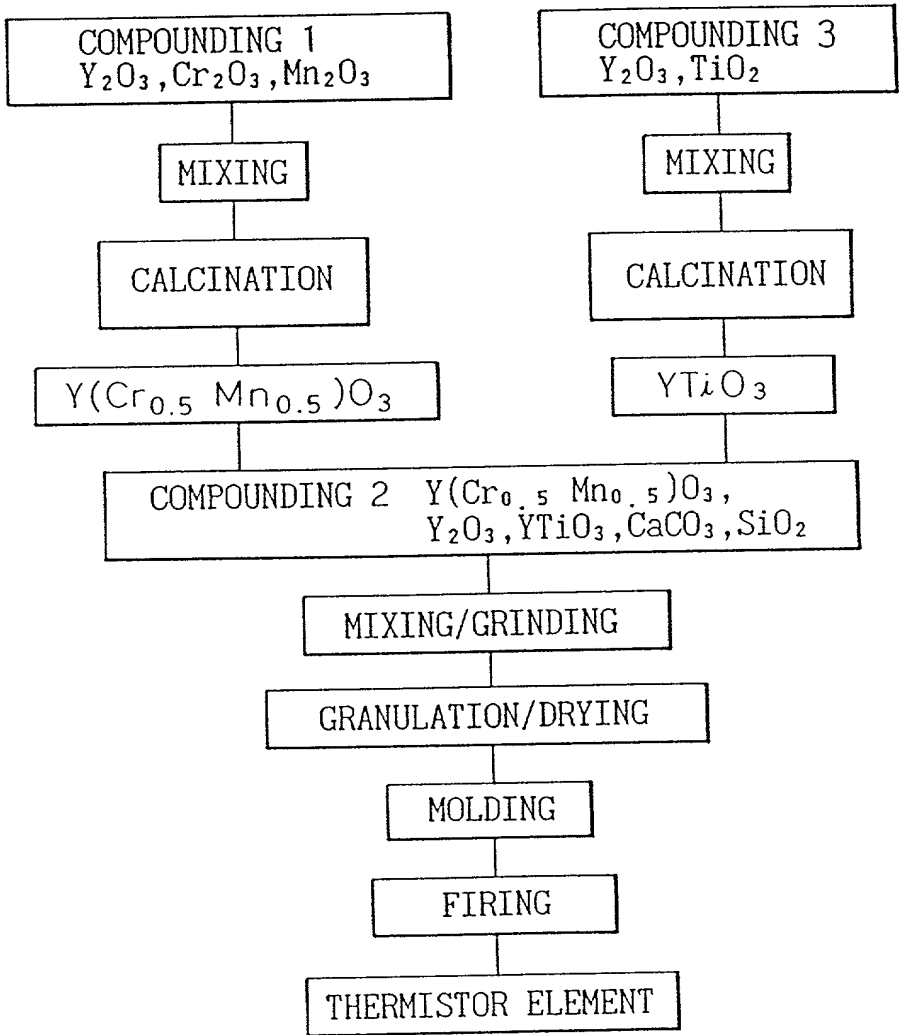


Fig. 8

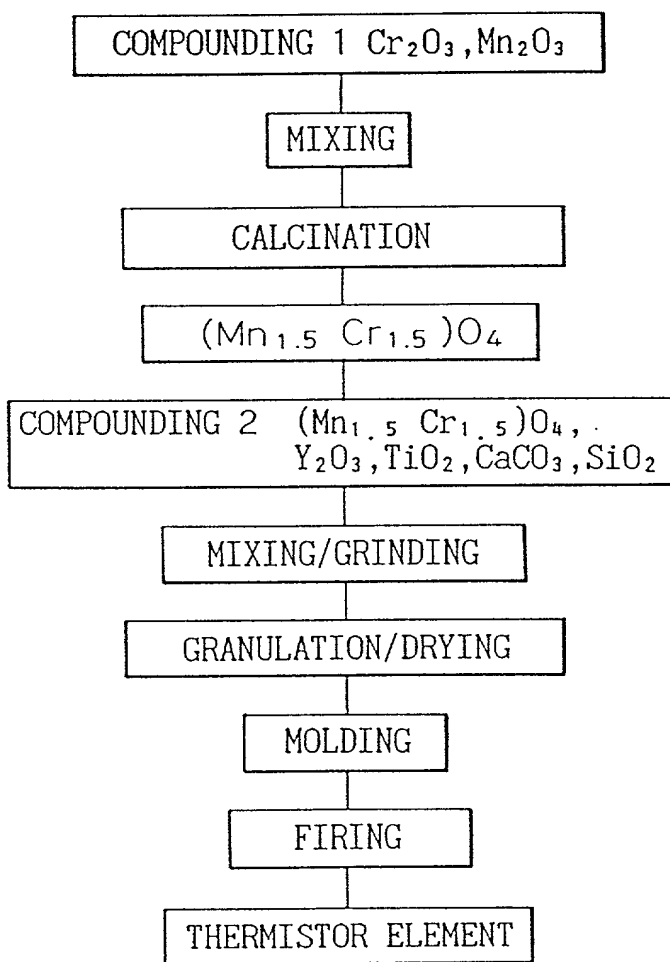
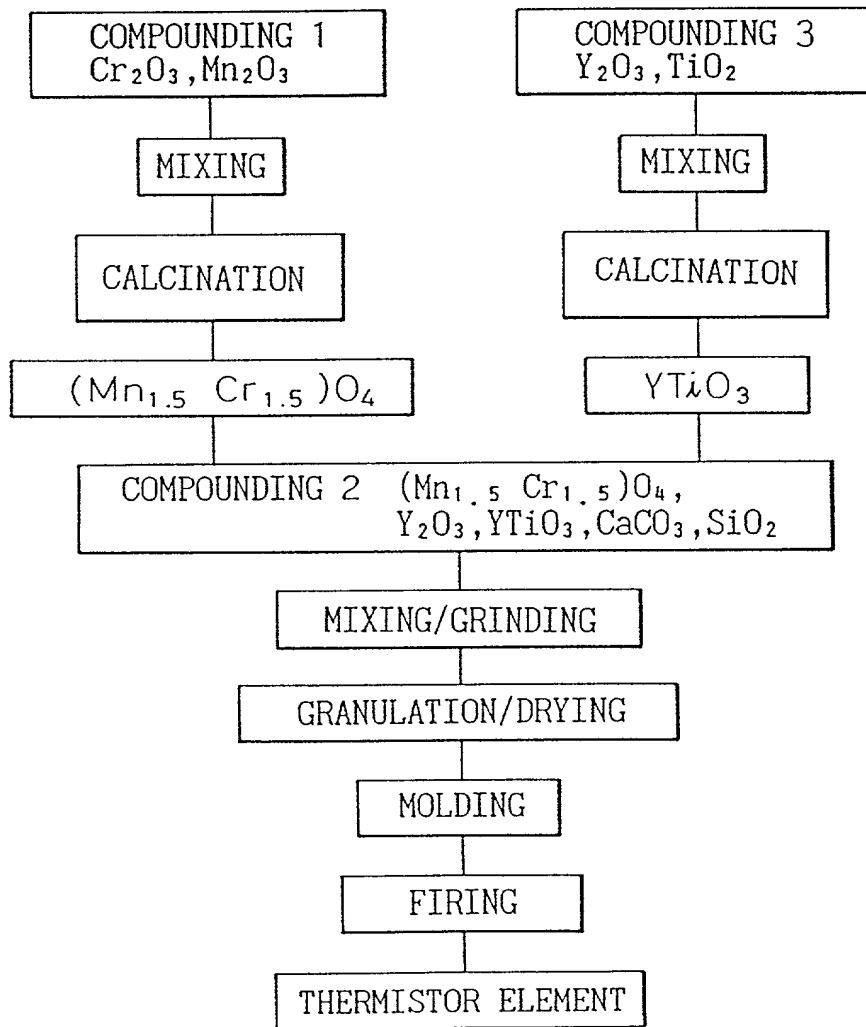


Fig. 9



Parameter	Value	Unit
Initial concentration of $\text{H}_2\text{O}_2$	0.01	M
Initial concentration of $\text{Fe}^{2+}$	0.001	M
Initial concentration of $\text{H}^+$	0.1	M
Temperature	25	$^\circ\text{C}$
Reaction time	0-100	min
Reaction rate constant $k$	0.001	$\text{min}^{-1}$
Reaction order	1	
Half-life $t_{1/2}$	69.3	min
Activation energy $E_a$	10.5	kJ/mol
Pre-exponential factor $A$	0.001	$\text{min}^{-1}$
Reaction mechanism	First-order reaction	
Rate of reaction	0.001	$\text{min}^{-1}$
Concentration of $\text{H}_2\text{O}_2$ at $t=0$	0.01	M
Concentration of $\text{H}_2\text{O}_2$ at $t=100$	0.005	M
Concentration of $\text{Fe}^{2+}$ at $t=0$	0.001	M
Concentration of $\text{Fe}^{2+}$ at $t=100$	0.0005	M
Concentration of $\text{H}^+$ at $t=0$	0.1	M
Concentration of $\text{H}^+$ at $t=100$	0.1	M
Reaction rate at $t=0$	0.001	$\text{min}^{-1}$
Reaction rate at $t=100$	0.0005	$\text{min}^{-1}$
Half-life $t_{1/2}$	69.3	min
Activation energy $E_a$	10.5	kJ/mol
Pre-exponential factor $A$	0.001	$\text{min}^{-1}$
Reaction mechanism	First-order reaction	
Rate of reaction	0.001	$\text{min}^{-1}$
Concentration of $\text{H}_2\text{O}_2$ at $t=0$	0.01	M
Concentration of $\text{H}_2\text{O}_2$ at $t=100$	0.005	M
Concentration of $\text{Fe}^{2+}$ at $t=0$	0.001	M
Concentration of $\text{Fe}^{2+}$ at $t=100$	0.0005	M
Concentration of $\text{H}^+$ at $t=0$	0.1	M
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Reaction rate at $t=0$	0.001	$\text{min}^{-1}$
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Concentration of $\text{H}^+$ at $t=0$	0.1	M
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Half-life $t_{1/2}$	69.3	min
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Reaction mechanism	First-order reaction	
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Concentration of $\text{H}_2\text{O}_2$ at $t=0$	0.01	M
Concentration of $\text{H}_2\text{O}_2$ at $t=100$	0.005	M
Concentration of $\text{Fe}^{2+}$ at $t=0$	0.001	M
Concentration of $\text{Fe}^{2+}$ at $t=100$	0.0005	M
Concentration of $\text{H}^+$ at $t=0$	0.1	M
Concentration of $\text{H}^+$ at $t=100$	0.1	M
Reaction rate at $t=0$	0.001	$\text{min}^{-1}$
Reaction rate at $t=100$		

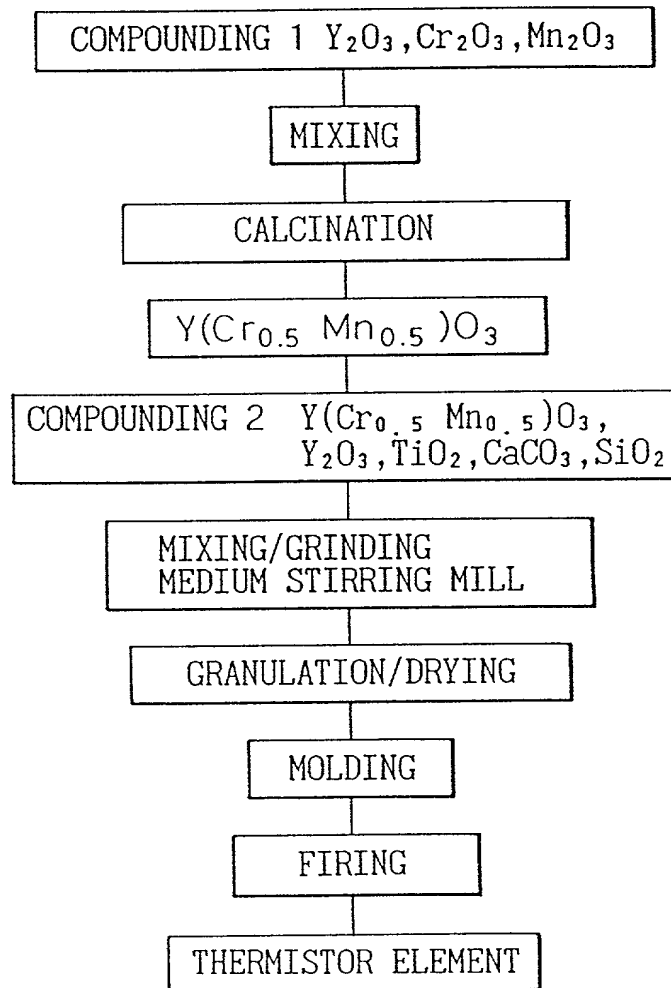


Fig. 11

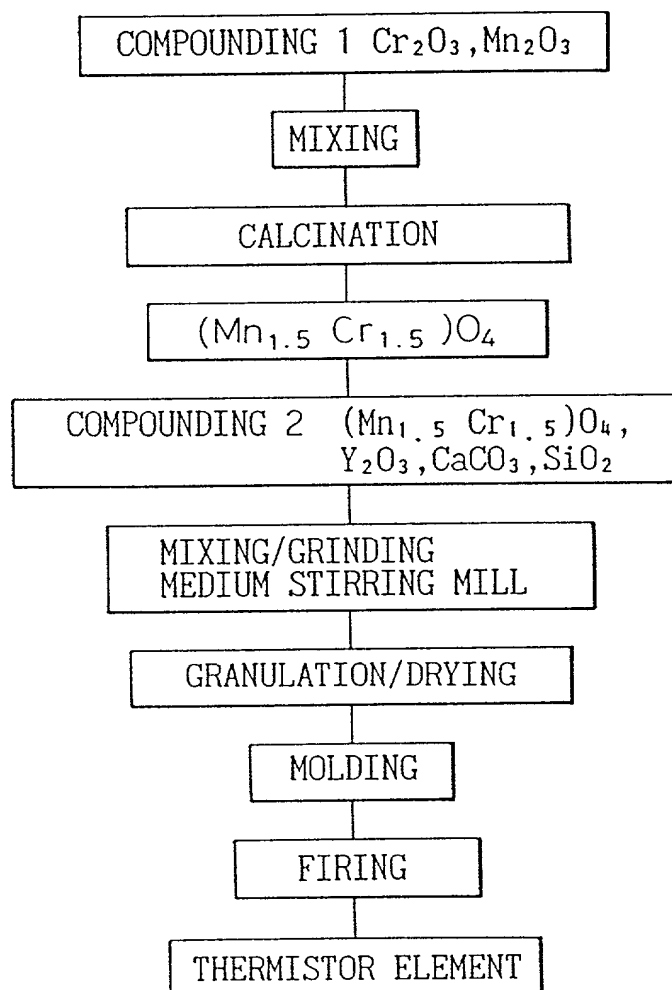


Fig .12

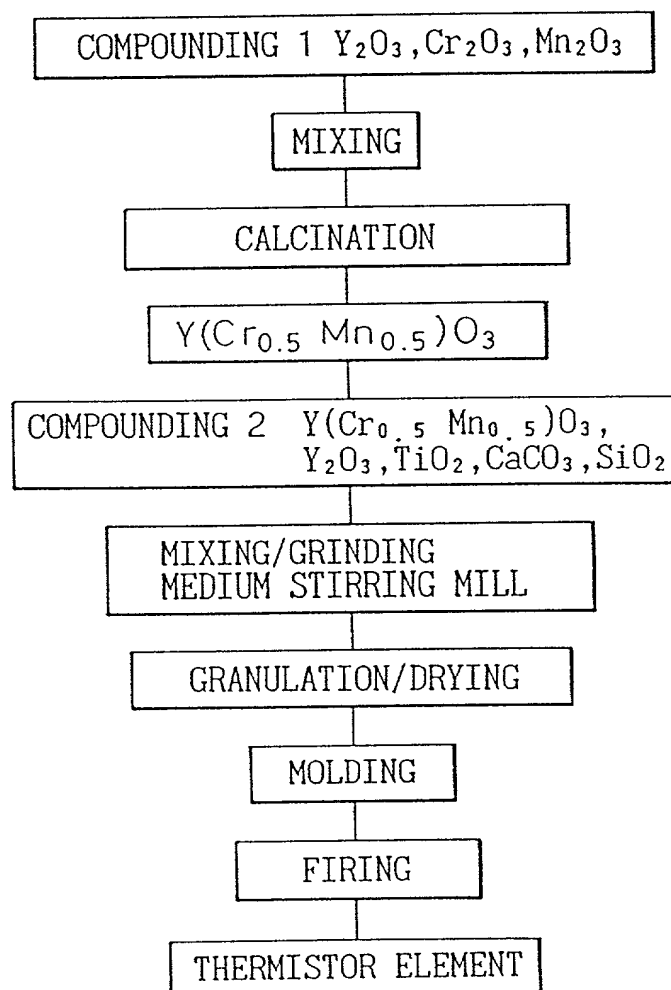


Fig. 13

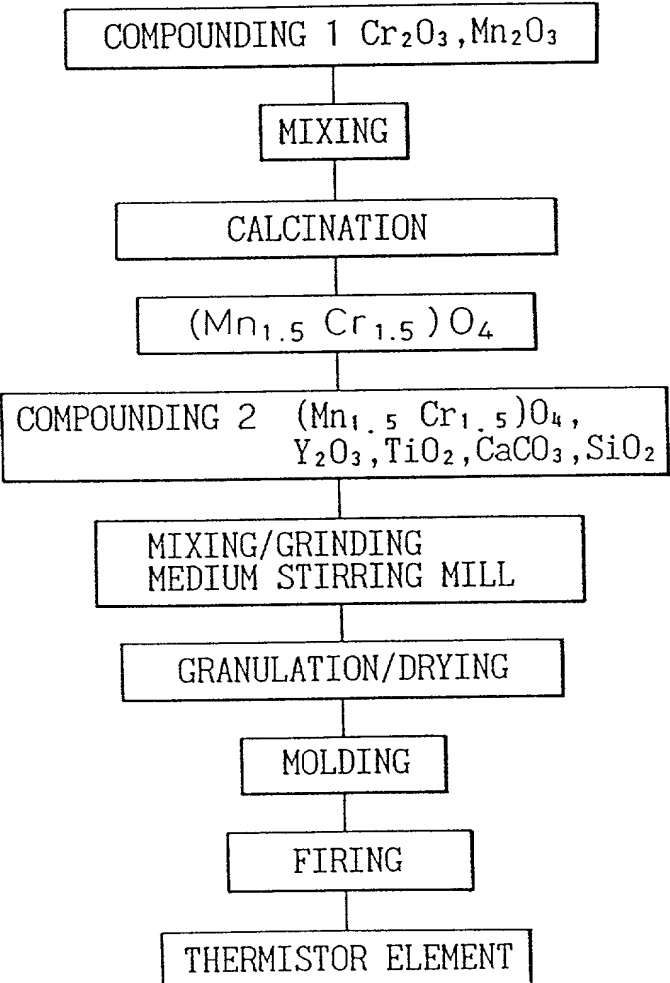


Fig. 14

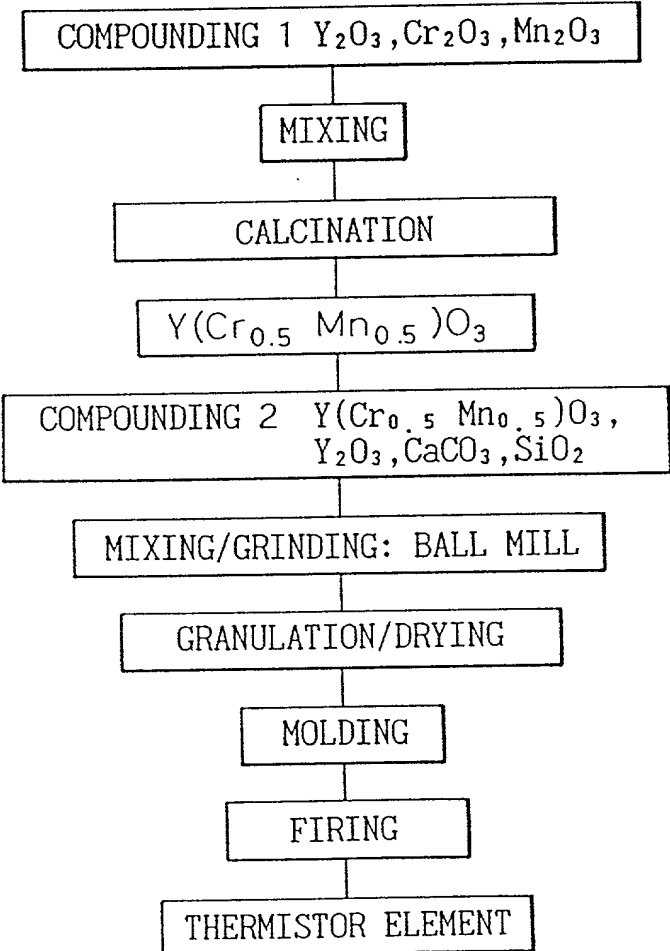




Fig.15

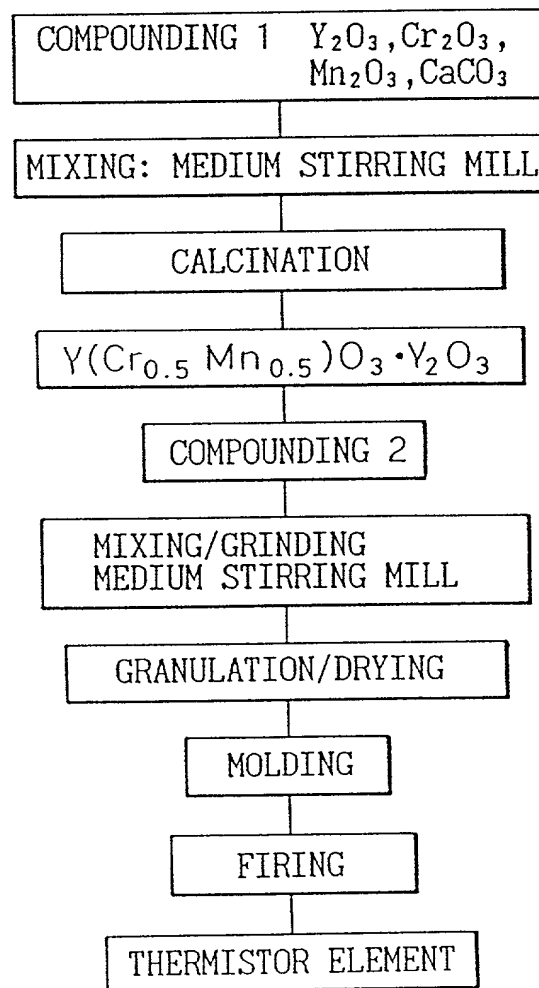


Fig. 16

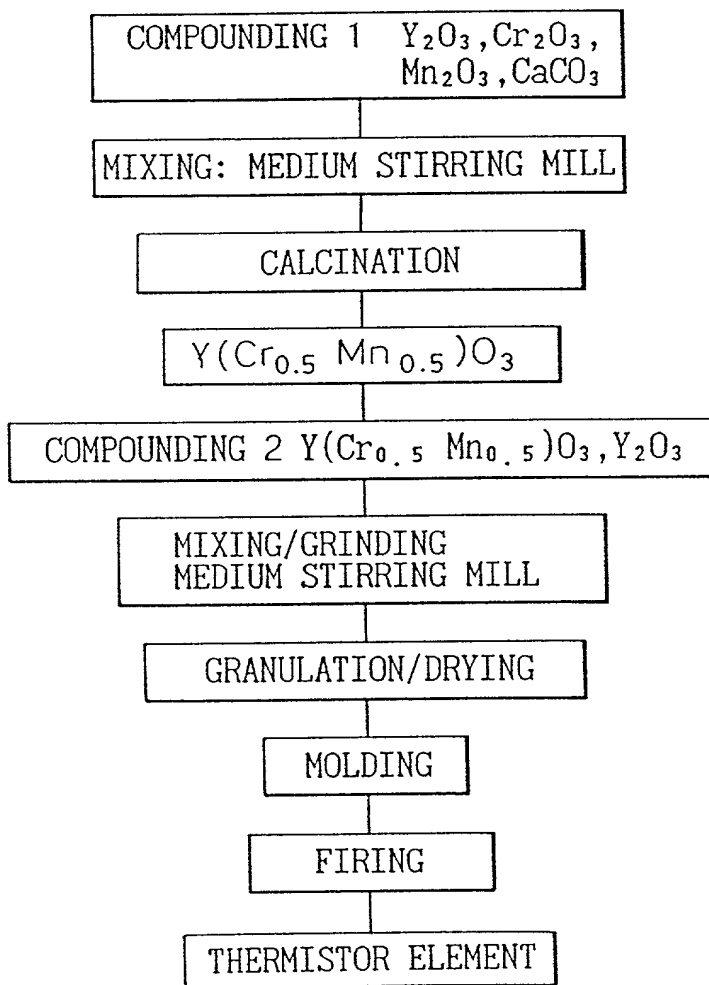


Fig .17

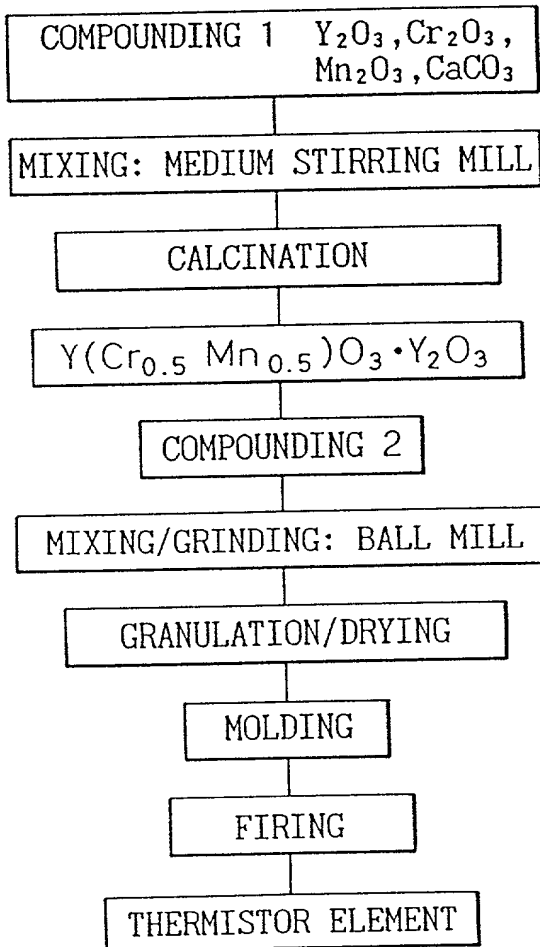


Fig .18

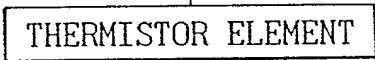


Fig.19

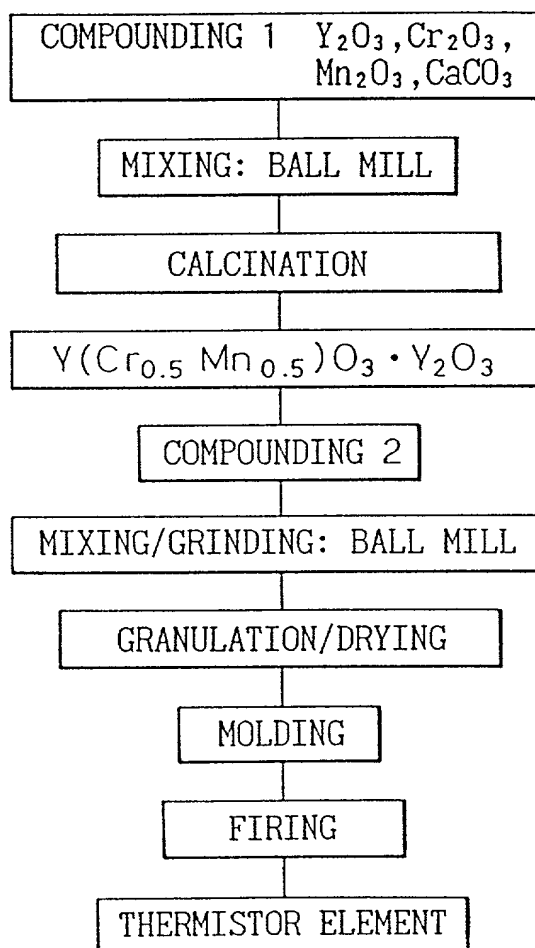


Fig. 20

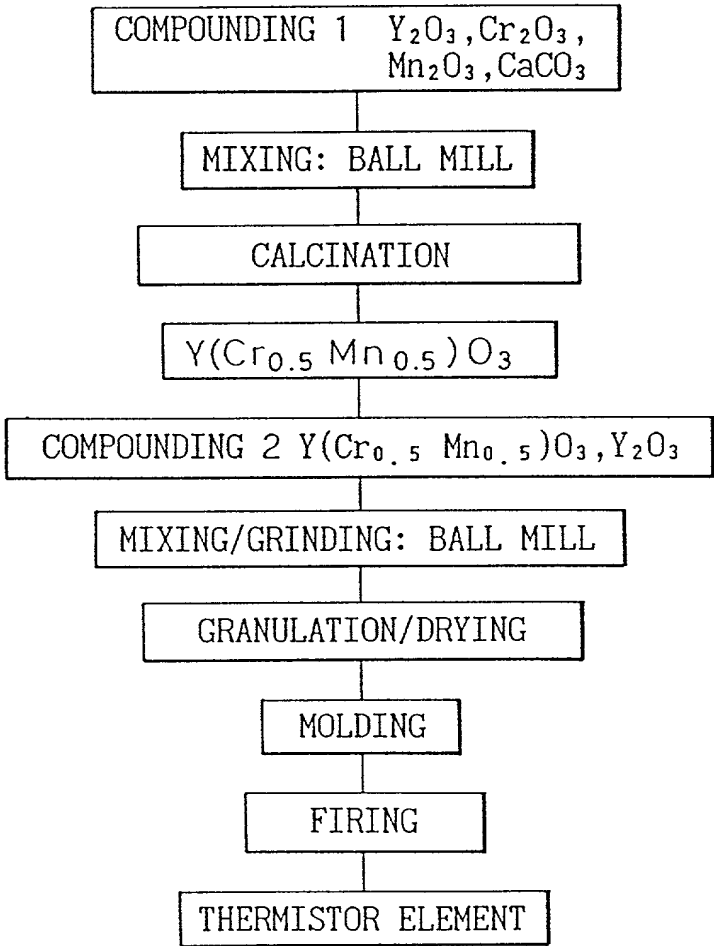


Fig. 21

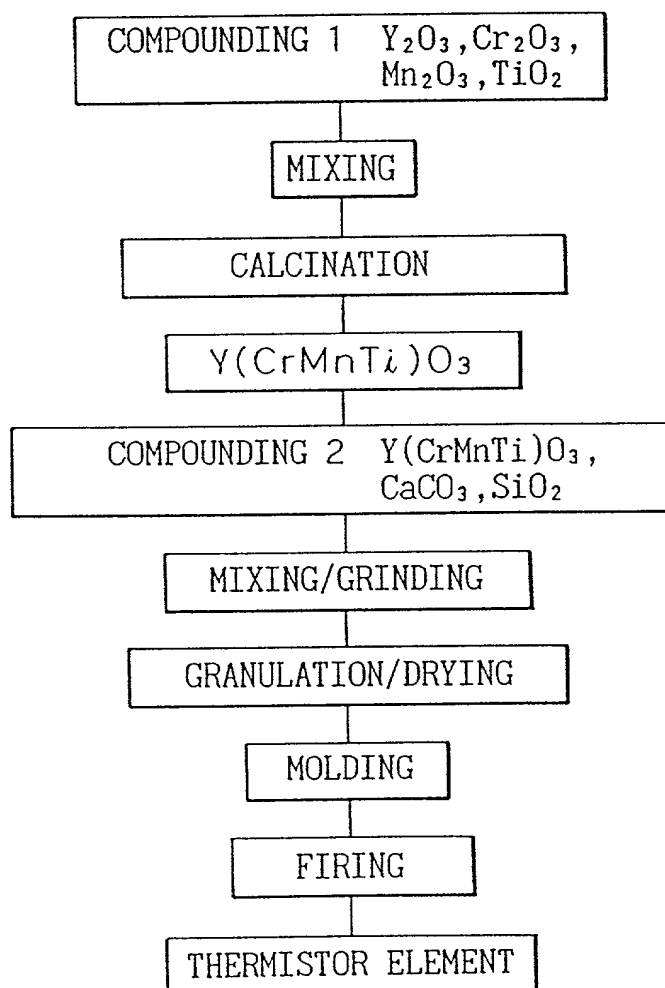


Fig. 22

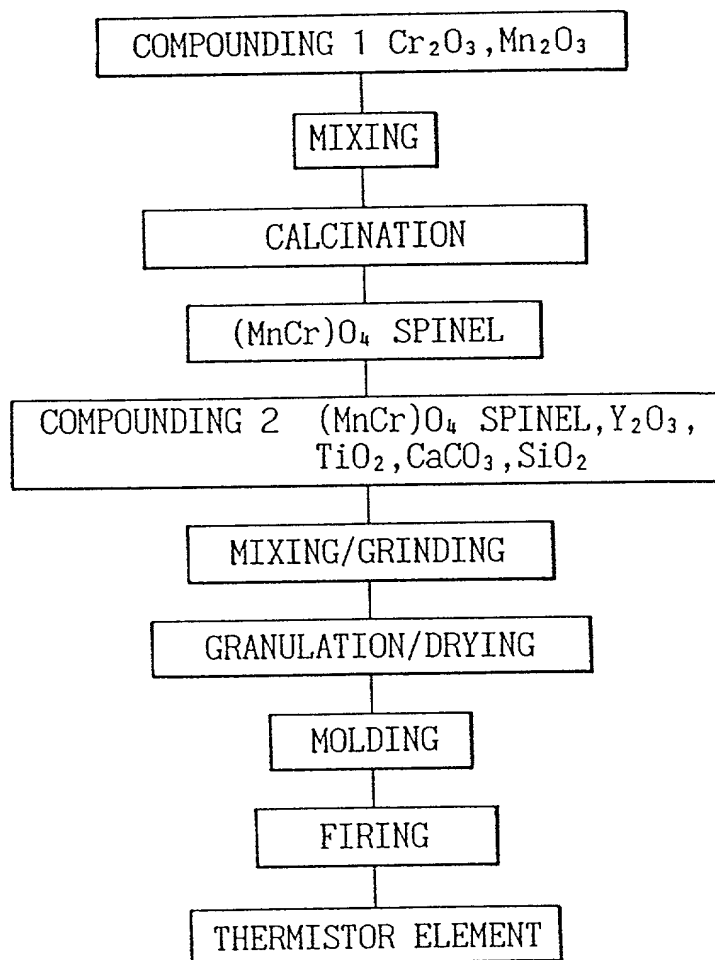




Fig. 23

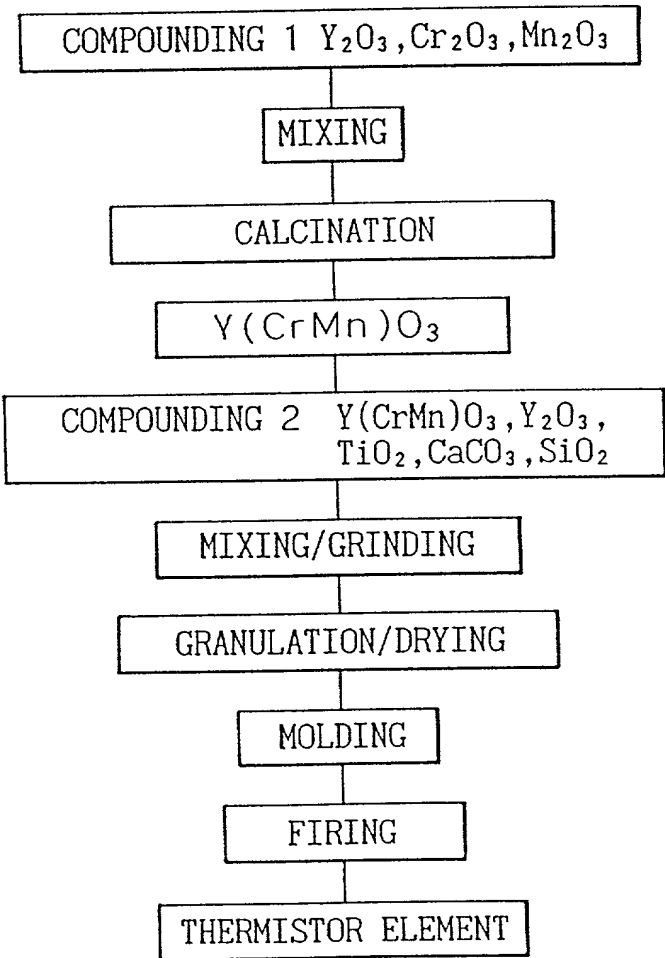


Fig. 24

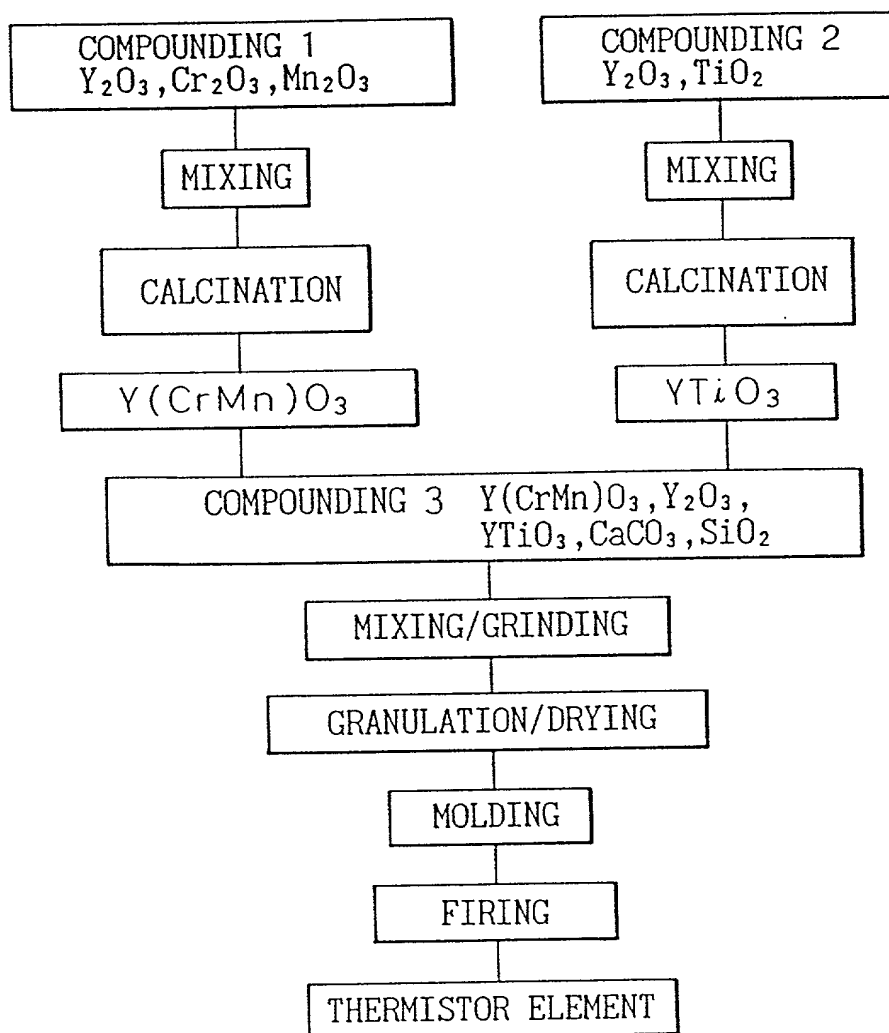
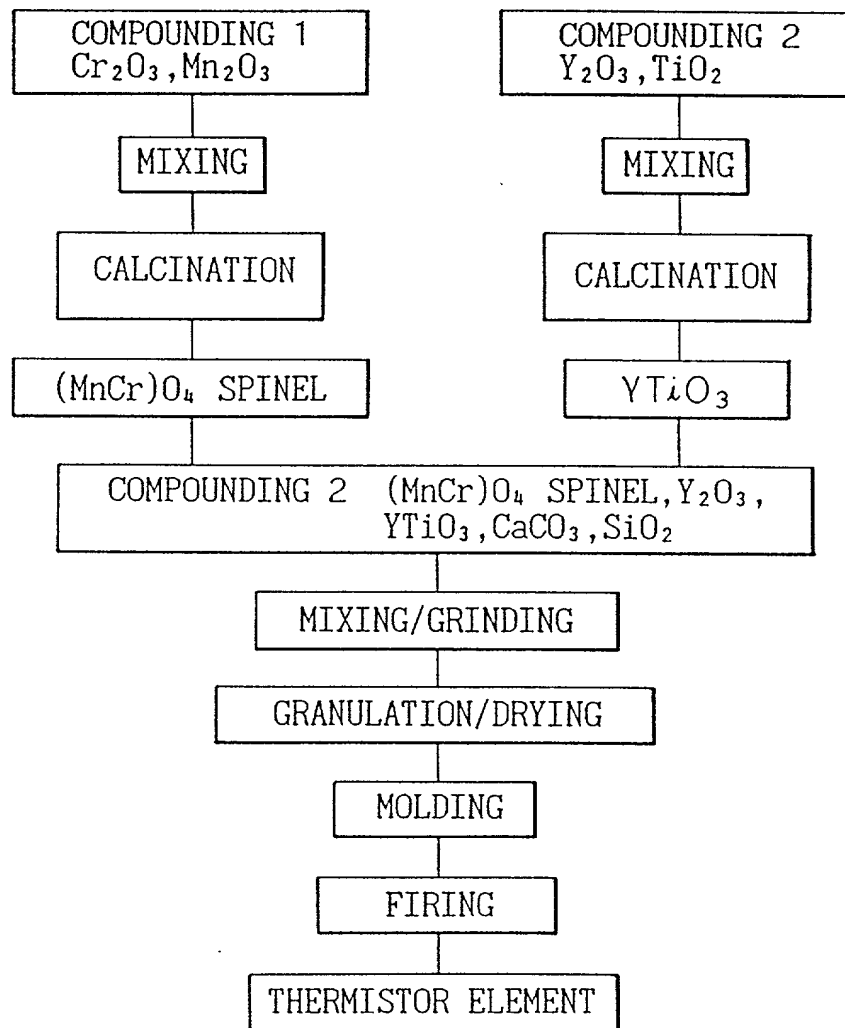


Fig .25



# Declaration and Power of Attorney For Patent Application

## 特許出願宣言書及び委任状

### Japanese Language Declaration

#### 日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

WIDE-RANGE TYPE THERMISTOR ELEMENT  
AND METHOD OF PRODUCING THE SAME

上記発明の明細書（下記の欄でx印がついていない場合は、本表に添付）は、

the specification of which is attached hereto unless the following box is checked:

☐ 月 日に提出され、米国出願番号または特許協定条約国際出願番号を \_\_\_\_\_ とし、  
（該当する場合） \_\_\_\_\_ に訂正されました。

☒ was filed on August 25, 1999  
as United States Application Number or  
PCT International Application Number  
\_\_\_\_\_ and was amended on  
\_\_\_\_\_ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されたとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

私は、米国法典第35編119条(a)-(d)項又は365条(b)項に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約365(a)項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

#### Prior Foreign Application(s)

外国での先行出願

<u>9-066827 (Pat. Appln.)</u>	<u>Japan</u>
(Number)	(Country)
(番号)	(国名)
<u>9-156931 (Pat. Appln.)</u>	<u>Japan</u>
(Number)	(Country)
(番号)	(国名)

<u>19/March/1997</u>
(Day/Month/Year Filed)
(出願年月日)
<u>13/June/1997</u>
(Day/Month/Year Filed)
(出願年月日)

Priority Not Claimed  
優先権主張なし

This application is a C-I-P application of serial No. 09/040,529 filed on March 18, 1998.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

# Japanese Language Declaration (日本語宣言書)

## Prior Foreign Application(s)

外国での先行出願

9-340313 (Pat. Appln.)	Japan
(Number)	(Country)
(番号)	(国名)
(Number)	(Country)
(番号)	(国名)
(Number)	(Country)
(番号)	(国名)
(Number)	(Country)
(番号)	(国名)

10/December/1997

(Day/Month/Year Filed)  
(出願年月日)

## Priority Not Claimed

優先権主張なし

☐

☐

☐

☐

私は、第35編米国法典119条(e)項に基づいて下記の米  
国特許出願規定に記載された権利をここに主張いたします。

I hereby claim the benefit under Title 35, United States Code,  
Section 119(e) of any United States provisional application(s) listed  
below.

(Application No.)  
(出願番号)

(Filing Date)  
(出願日)

(Application No.)  
(出願番号)

(Filing Date)  
(出願日)

私は、下記の米国法典第35編120条に基づいて下記の米  
国特許出願に記載された権利、又は米国を指定している特許  
協力条約365条(c)に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条  
第1項又は特許協力条約で規定された方法で先行する米国特  
許出願に開示されていない限り、その先行米国出願書提出日  
以降で本出願書の日本国内または特許協力条約国際提出日ま  
での期間中に入手された、連邦規則法典第37編1条56項  
で定義された特許資格の有無に関する重要な情報について開  
示義務があることを認識しています。

I hereby claim the benefit under Title 35, United States Code,  
Section 120 of any United States application(s), or 365(c) of any  
PCT International application designating the United States, listed  
below and, insofar as the subject matter of each of the claims of  
this application is not disclosed in the prior United States or PCT  
International application in the manner provided by the first  
paragraph of Title 35, United States Code Section 112, I  
acknowledge the duty to disclose information which is material to  
patentability as defined in Title 37, Code of Federal Regulations,  
Section 1.56 which became available between the filing date of the  
prior application and the national or PCT International filing date of  
application.

09/040,529

March 18, 1998

Pending

(Application No.)  
(出願番号)

(Filing Date)  
(出願日)

(Status: Patented, Pending, Abandoned)  
(現況: 特許許可済、係属中、放棄済)

(Application No.)  
(出願番号)

(Filing Date)  
(出願日)

(Status: Patented, Pending, Abandoned)  
(現況: 特許許可済、係属中、放棄済)

私は、私自身の知識に基づいて本宣言書中で私が行なう表  
明が真実であり、かつ私の入手した情報と私の信じているところ  
に基づく表明が全て真実であると信じていること、さらに故  
意になされた虚偽の表明及びそれと同等の行為は米国法典第  
18編第1001条に基づき、罰金または拘禁、もしくはそ  
の両方により処罰されること、そしてそのような故意による  
虚偽の声明を行なえば、出願した、又は既に許可された特許  
の有効性が失われることを認識し、よってここに上記のごと  
く宣誓を致します。

I hereby declare that all statements made herein of my own  
knowledge are true and that all statements made on information  
and belief are believed to be true; and further that these  
statements were made with the knowledge that willful false  
statements and the like so made are punishable by fine or  
imprisonment, or both, under Section 1001 of Title 18 of the  
United States Code and that such willful false statements may  
jeopardize the validity of the application or any patent issued  
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### Japanese Language Declaration (日本語宣言書)

委任状: 私は下記の発明者として、本出願に関する一切の  
手続きを米特許商標局に対して遂行する弁理士または代理人  
として、下記の者を指名いたします。(弁理士、または代理  
人の氏名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint  
the following attorney(s) and/or agent(s) to prosecute this  
application and transact all business in the Patent and Trademark  
Office connected therewith (list name and registration number)

And I hereby appoint Pillsbury Madison & Sutro LLP, Intellectual Property Group, 1100 New York Avenue, N.W., Ninth Floor, East Tower, Washington, D.C. 20005-3918, telephone number (202) 861-3000 (to whom all communications are to be directed), and the below-named persons (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to delete names/numbers below of persons no longer with their firm and to act and rely on instructions from and communicate directly with the person/assignee/attorney/firm/ organization who/which first sends/sent this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct the above Firm and/or a below attorney in writing to the contrary.

Paul N. Kokulis	16773	David W. Brinkman	20817	Paul E. White, Jr.	32011	Stephen C. Glazier	31361
Raymond F. Lippitt	17519	George M. Sirilla	18221	Michelle N. Lester	32331	Paul F. McQuade	31542
G. Lloyd Knight	17698	Donald J. Bird	25323			Ruth N. Morduch	31044
Carl G. Love	18781		25647	G. Paul Edgell	24238	Richard H. Zaiden	27248
Edgar H. Martin	20534	Peter W. Gowdey	25872	Lynn E. Eccleston	35861	Roger R. Wise	31204
William K. West, Jr.	22057	Dale S. Lazar	28872	David A. Jakopin	32995		
Kevin E. Joyce	20508	Glenn J. Perry	28458	Mark G. Paulson	30793		
		Kendrew H. Colton	30368	Timothy J. Klima	34852		

唯一または第一発明者名	Full name of sole or first inventor	Itsuhei Ogata	
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		<i>Itsuhei Ogata</i>	<i>Sept. 1, 1999</i>
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私書箱	Post Office Address	c/o NIPPON SOKEN, INC., 14, Iwaya, Shimohasumi-cho, Nishio-shi, Aichi, Japan	
第二共同発明者	Full name of second joint inventor, if any	Takumi Kataoka	
第二共同発明者	日付	Second inventor's signature	Date
		<i>Takumi Kataoka</i>	<i>Sep 1 1999</i>
住所	Residence	Nishio-shi, Aichi, Japan	
国籍	Citizenship	Japanese	
私書箱	Post Office Address	c/o NIPPON SOKEN, INC., 14, Iwaya, Shimohasumi-cho, Nishio-shi, Aichi, Japan	

(第三以降の共同発明者についても同様に記載し、署名をす  
ること)

(Supply similar information and signature for third and subsequent  
joint inventors.)

097634743000

第三共同発明者	Full name of third joint inventor, if any Eturo Yasuda		
第三共同発明者	日付	Third inventor's signature <i>Eturo Yasuda</i>	Date <i>Sept 1, 1999</i>
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国 籍	Citizenship Japanese		
私書箱	Post Office Address c/o NIPPON SOKEN, INC., 14, Iwaya, Shimohasumi-cho, Nishio-shi, Aichi, Japan		
第四共同発明者	Full name of fourth joint inventor, if any Kaoru Kuzuoka		
第四共同発明者	日付	Fourth inventor's signature <i>Kaoru Kuzuoka</i>	Date <i>Sept 1, 1999</i>
住 所	Residence Toyota-shi, Aichi, Japan		
国 籍	Citizenship Japanese		
私書箱	Post Office Address c/o DENSO CORPORATION 1-1 SHOWA-CHO KARIYA-CITY AICHI-PREF. 448-8661 Japan		

第五共同発明者	Full name of fifth joint inventor, if any Masanori Yamada		
第五共同発明者	日付	Fifth inventor's signature <i>Masanori Yamada</i>	Date <i>Sept 1, 1999</i>
住 所	Residence Nishio-shi, Aichi, Japan		
国 籍	Citizenship Japanese		
私書箱	Post Office Address c/o NIPPON SOKEN, INC., 14, Iwaya, Shimohasumi-cho, Nishio-shi, Aichi, Japan		
第六共同発明者	Full name of sixth joint inventor, if any		
第六共同発明者	日付	Sixth inventor's signature	Date
住 所	Residence		
国 籍	Citizenship		
私書箱	Post Office Address		

(第七以降の共同発明者についても同様に  
記載し、署名をすること)

(Supply similar information and signature for  
seventh and subsequent joint inventors.)